

# **PHOTOCHEMICAL REARRANGEMENTS OF A FEW SELECTED HETEROCYCLES**

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of

**DOCTOR OF PHILOSOPHY**

*by*

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*to the*

**DEPARTMENT OF CHEMISTRY**

**INDIAN INSTITUTE OF TECHNOLOGY, KANPUR**

**FEBRUARY, 1987**

*Dedicated*

*To*

*My Parents*

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CERTIFICATE OF COURSE WORK

This is to certify that Mr. K. R. Gopidas has satisfactorily completed all the courses required for the Ph.D. programme. These courses include :

Chm 502 Advanced Organic Chemistry II  
Chm 505 Principles of Organic Chemistry  
Chm 521 Chemical Binding  
Chm 524 Modern Physical Methods in Chemistry  
Chm 525 Principles of Physical Chemistry  
Chm 545 Principles of Inorganic Chemistry  
Chm 800 General Seminar  
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Chm 900 Post-Graduate Research

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Certified that the work embodied in this thesis entitled: 'PHOTOCHEMICAL REARRANGEMENTS OF A FEW SELECTED HETEROCYCLES' has been carried out by Mr. K. R. Gopidas, under my supervision and the same has not been submitted elsewhere for a degree.

  
M. V. George  
Thesis Supervisor

## STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor M. V. George.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



K. R. Gopidas

## ACKNOWLEDGEMENTS

It is with great pleasure that I place on record my deep sense of gratitude to Professor M. V. George for suggesting the research problem and for encouraging me to a successful completion of this work. Also, I wish to express my thanks to Dr. P. K. Das of the Radiation Laboratory of the University of Notre Dame, for carrying out the laser flash photolysis and fluorescence studies, reported in this thesis.

My sincere thanks are due to Professor P. S. Goel, Professor S. Chandrasekaran and all other members of the Chemistry faculty for their encouragement and interest in my progress.

Of a number of colleagues in the Department of Chemistry who have been of valuable help to me, I would like to make special mention of Drs. C. V. Kumar, P. M. Scaria, B. B. Lohray, B. A. R. C. Murty, E. J. Dominic, R. K. Tikare and J. S. Biradar. Mention may also be made of Messrs S. Prathapan, K. Ashok, D. Ramaiah, M. Muneer, R. Barik, P. J. Sajan, V. K. Sankaranarayanan and C. Santhosh Kumar.

My thanks are due to the Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, and the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow, for recording some

of the NMR and Mass Spectra reported in this thesis. Special mention may be made of Mr. P. R. Rajmohan (National Chemical Laboratories, Pune) for recording some of the NMR spectra reported in this thesis.

I sincerely acknowledge the help rendered by Mr. K. Rajagopalan, Mr. N. Ahmed and the staff of the Chemistry Departmental Office, Chemistry Stores, Chemistry Workshop, Central Library, Central Glass Blowing Workshop and Graphic Arts Section. My sincere thanks are due to Mr. B. L. Shyamal for his ready and unreserved help throughout my stay here.

I wish to express my appreciation and thanks to Mr. C. M. Abraham for the typing of the thesis, Mr. R. K. Bajpai for the drawings and Mr. Mumtaz Ahmed for binding.

Financial assistance from the authorities of I.I.T., Kanpur in the form of a Research Assistantship is gratefully acknowledged.

Finally, I wish to express my indebtedness and gratitude to my parents, brothers and sisters for their constant support and encouragement.

Kanpur  
February, 1987

K. R. Gopidas

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## PREFRACE

The thesis entitled: 'Photochemical Rearrangements of a Few Selected Heterocycles' consists of three chapters.

Chapter I deals with our studies on the phototransformations of several 3,3,5-triaryl-2(3H)-furanones. Some of the compounds that we have examined include 3,3,5-triphenyl-2(3H)-furanone (5a), 3,5-diphenyl-3-(4-methylphenyl)-2(3H)-furanone (5b), 3,5-diphenyl-3-(4-methoxyphenyl)-2(3H)-furanone (5c), 3-(4-cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d) and 3-(4-chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e).

Irradiation of the 2(3H)-furanones 5a-e in benzene and methanol gave the corresponding decarbonylated products 6a-e in good yields, along with small amounts of the unchanged starting material, in each case. In contrast, sensitized irradiations of 5a-e in benzene, using acetophenone gave a mixture of the photorearranged 2(5H)-furanones 7a-e and 10b,c along with the corresponding phenanthrofurane derivatives 9a-e and 11b,c, respectively. Based on product analysis, p-chlorophenyl, p-cyanophenyl and p-tolyl groups were found to be better migrating groups from C-3 carbon compared to phenyl, whereas p-anisyl group was found to have a lesser migratory aptitude

than phenyl. The observed migratory aptitudes, as well as the formation of the methanol adduct 23 in the acetophenone sensitized irradiation of 5a in methanol suggest the involvement of intermediates having significant ionic character. Laser flash photolysis studies of the direct irradiations of 5a-e suggest that the two-bond cleavage resulting in the photoextrusion of CO takes place in a concerted manner from the singlet excited states of these molecules. Laser flash photolysis studies of the sensitized reactions of 5a-e have enabled us to observe the triplets of these substrates which have lifetimes in the submicrosecond time domain. From these studies, the aryl group migrating abilities were estimated at  $1.5 \times 10^6 \text{ s}^{-1}$ , except for the p-cyanophenyl group for which the rate is higher by one order of magnitude. Reasonable mechanisms have been suggested for the formation of the various products in these reactions.

Our studies on the photochemical, thermal and photoinduced electron-transfer reactions of a few 3-benzyl-3,5-diaryl-2(3H)-furanones and related substrates form the subject matter of Chapter II of the thesis. The substrates studied in this connection include 3-benzyl-3,5-diphenyl-2(3H)-furanone (2a), 3-benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b), 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone (2c), 3,3-dibenzyl-5-phenyl-2(3H)-furanone (2d), 3-benzyl-3-phenyl-

phenanthro[9,10-b]furan-2(3H)-one (9), 3-benzoyl-3,5-diphenyl-2(3H)-furanone (15), 5,5'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18b) and 6,6'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18c).

Irradiation of the furanones 2a-d in benzene and methanol gave the corresponding 2,3,5-triarylfuran derivatives 7a-c (except in the case of 2d) and the butenone derivatives 8a-d, along with the recovery of some amounts of the starting material in each case. In contrast, irradiation of 2a-d in benzene in the presence of acetophenone gave the rearranged 2(5H)-furanones 13a-d and the bisfuranones 14a-c (except in the case of 2d), along with some amount of the unchanged starting material. Irradiation of the phenanthrofurane 9 in benzene and methanol gave the phenanthrofurane 10, whereas irradiation of the benzoylfuranone 15 in benzene and methanol gave the bisfuranone 14a. Thermolysis of the furanones 2a-d also gave the rearranged 2(5H)-furanones 13a-d. Photoinduced electron-transfer reactions of 2a,b, on the other hand, gave the bisfuranones 14a,b, whereas the related bis(benzofuranones) 18b,c, under similar conditions, gave the benzofuranones 22b,c and the hydroxy furanones 24b,c, along with some recovered starting material. Laser flash photolysis studies of the photoinduced electron-transfer reactions of the 2(3H)-furanones 2a-c and



the bis(benzofuranones) 18a-d suggest that the radical cations from these substrates undergo fragmentation to the furanoxo radicals and the corresponding cations, on a nanosecond time scale. For the purpose of identification, these furanoxo radicals have been generated through hydrogen abstraction by photogenerated tert-butoxy radical from 2(5H)-furanones 1a-c and the benzofuranone 22a, as well as via direct photolysis of 3-benzoyl-3,5-diphenyl-2(3H)-furanone (15). Reasonable mechanisms have been suggested for the formation of the various products in these reactions.

Chapter III of the thesis deals with our studies on the photochemical ring enlargement reactions of a few 2H-1,2,4-benzothiadiazine-2-aryl-3-methyl 1,1-dioxides. The substrates that we have studied include 2H-1,2,4-benzothiadiazine-2-(4-methoxyphenyl)-3-methyl 1,1-dioxide (4b), 2H-1,2,4-benzothiadiazine-2-(4-carbomethoxyphenyl)-3-methyl 1,1-dioxide (4c), 2H-1,2,4-benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-dioxide (4d) and 2H-1,2,4-benzothiadiazine-2-(2,6-dimethylphenyl)-3-methyl 1,1-dioxide (4e).

Irradiation of the benzothiadiazine dioxides 4b-d in benzene and methanol gave moderate yields (14-70%) of 5H-dibenzo[b,g][1,4,6]thiadiazocine dioxides 9b,d, along with some

amounts of the unchanged starting material, in each case. Upon sensitized irradiation in benzene using acetophenone, 4b gave the ring enlarged product 9b in 40% yield. In contrast, irradiation of 4e in benzene or acetone gave a ring opened product 10. Laser flash photolysis of the thiadiazine dioxides under direct excitation gave long-lived transients, characterized by weak absorptions at 315-420 nm. Both benzophenone and p-methoxyacetophenone triplets were quenched by the benzothiadiazine dioxides with rate constants  $(0.58-7.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Reasonable mechanisms have been suggested for the formation of the ring enlargement products in these reactions.

Note : The numbers of the various compounds given here correspond to those given under the respective chapters.

## CHAPTER I

### PHOTOTRANSFORMATIONS OF 3,3,5-TRIARYL-2(3H)-FURANONES

#### I.1 ABSTRACT

The photochemical transformations of a few 3,3,5-tri-aryl-2(3H)-furanones such as 3,3,5-triphenyl-2(3H)-furanone (5a), 3,5-diphenyl-3-(4-methylphenyl)-2(3H)-furanone (5b), 3,5-diphenyl-3-(4-methoxyphenyl)-2(3H)-furanone (5c), 3-(4-cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d) and 3-(4-chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e) have been examined in the present studies. These furanones 5a-e were prepared by the thermolysis of the corresponding 1,2,4-triaryl-but-2-en-1,4-diones 15a-e.

Irradiation of the 2(3H)-furanones 5a-e in benzene or methanol gave the corresponding decarbonylated products 6a-e in good yields, along with small amounts of the recovered starting material. In contrast, sensitized irradiations of 5a-e in benzene using acetophenone gave a mixture of the photorearranged 2(5H)-furanones 7 and 10, along with the corresponding phenanthrofuranone derivatives 9 and 11, respectively. Based on product analysis, p-chlorophenyl, p-cyanophenyl and p-tolyl groups were found to be better migrating groups (from C-3 carbon) compared to phenyl,

whereas p-anisyl group was found to have a lesser migratory aptitude than phenyl.

The preferential migration of the p-chloro- and p-cyanophenyl groups over phenyl and of phenyl group over p-anisyl in the sensitized irradiations, as well as the formation of the methanol adduct 23 in the acetophenone sensitized irradiation of 5a in methanol, suggest the involvement of intermediates having significant ionic character.

Laser flash photolysis studies of the direct irradiations of 5a-e indicated that the two-bond cleavage resulting in the photoextrusion of CO takes place in a concerted manner from the singlet excited states of these molecules. Laser flash photolysis studies of the sensitized reactions of 5a-e enabled us to observe the triplets of these substrates, which have lifetimes in the submicrosecond time domain. From these studies, the migratory abilities of aryl groups were estimated at  $1.5 \times 10^6 \text{ s}^{-1}$ , except for the p-cyanophenyl group for which the rate is higher by one order of magnitude.

## 1.2 INTRODUCTION

Photochemical transformations of five-membered unsaturated lactones such as 2(3H)-furanones and 2(5H)-furanones have been investigated in detail.<sup>1-19</sup> Some of the major reaction pathways

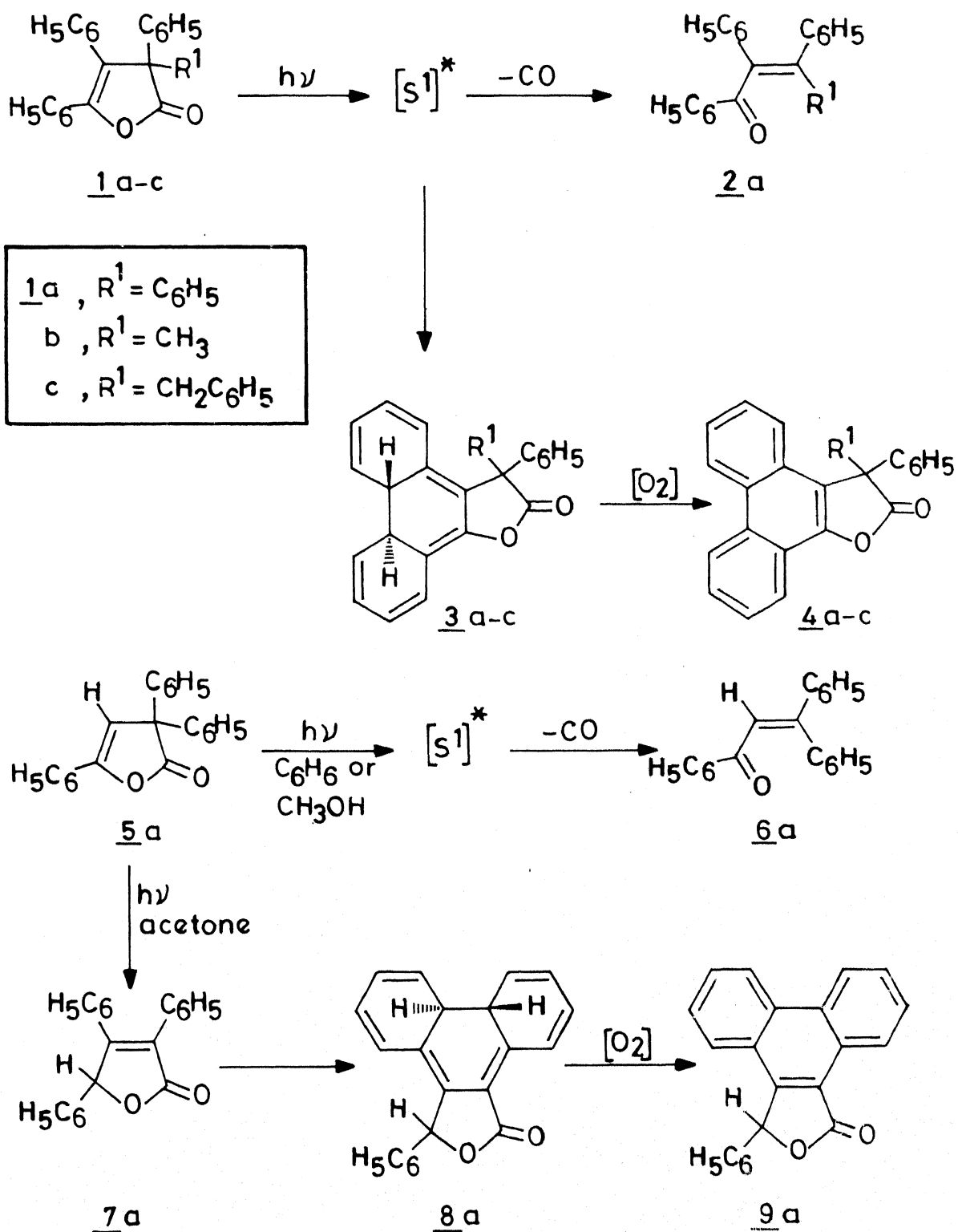
of these furanones under photochemical conditions include decarbonylation,<sup>2,3,7,19</sup> decarboxylation,<sup>4</sup> solvent addition to double bonds,<sup>8,10,14,15</sup> migration of aryl substituents,<sup>15</sup> and dimerization.<sup>11,17</sup> In the case of 2(3H)-furanones, for example, Chapman and McIntosh have previously suggested that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is the presence of a double bond adjacent to the ether oxygen which can stabilize the incipient radical centre at the oxygen atom.<sup>7</sup> The stabilized diradical can subsequently lose carbon monoxide to give  $\alpha,\beta$ -unsaturated ketones. However, the possibility of these reactions proceeding through a concerted pathway involving excited singlet state species could not be ruled out. Similar photochemical decarbonylation reactions have been observed in several other related substrates such as lactams,<sup>20,21</sup> thiolactones,<sup>22,23</sup> sultones,<sup>7</sup> carbonates,<sup>3</sup> and some indanone derivatives.<sup>24</sup> Besides decarbonylation, dimerization and the formation of chromone derivatives have also been observed in the case of 2(3H)-furanones.<sup>17,25</sup> Padwa and co-workers<sup>26-28</sup> have shown that the phototransformations of benzo[b]-2(3H)-furanones lead to a variety of products, arising through quinone methide intermediates.

The photochemical and thermal transformations of a number of 2(3H)-furanones and bis(benzofuranones) have been recently

reported from this laboratory.<sup>30,31</sup> The two prominent pathways for the photoreactions of these 2(3H)-furanones include a singlet-mediated decarbonylation to give  $\alpha,\beta$ -unsaturated carbonyl compounds and cyclization involving the 4- and 5-phenyl groups to give 4a,4b-dihydrophenanthrenes (Scheme I.1). Thus, 3,3,4,5-tetraphenyl-2(3H)-furanone (1a) upon irradiation in benzene or methanol gave the decarbonylated product 2a in major amounts, along with the phenanthrene derivative 4a, in small amounts. However, the 2(3H)-furanones 1b and 1c, under analogous conditions, gave the phenanthrofuranone derivatives 4b and 4c, respectively, as the only isolable product. In contrast, the furanone 5a, which is unsubstituted at the 4-position gave only the decarbonylated product under direct irradiation. However, sensitized irradiation of 5a leads to an interesting photorearrangement to give the 2(5H)-furanone 7a and the phenanthrofuranone 9a.

In the present study, we have examined in detail, the sensitized photorearrangements of several 3,3,5-triaryl-2(3H)-furanones. These furanones, in principle, should give two 2(5H)-furanones arising through the migration of either of the aryl groups from C-3 to C-4 position; the ease of migration being controlled by the migratory aptitude of the aryl groups. Thus, the objective of the present study has been

# Scheme 1.1



to examine the excited-state migratory aptitudes of the different aryl groups in this photorearrangement and also to characterize the intermediates involved in these reactions by using laser flash spectroscopy. The 2(3H)-furanones that we have examined include 3,3,5-triphenyl-2(3H)-furanone (5a), 3,5-diphenyl-3-(4-methylphenyl)-2(3H)-furanone (5b), 3,5-diphenyl-3-(4-methoxyphenyl)-2(3H)-furanone (5c), 3-(4-cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d) and 3-(4-chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e).

### I.3 RESULTS AND DISCUSSION

I.3.1 Preparation of Starting Materials. The 2(3H)-furanones that we have employed in the present studies, namely, 3,3,5-triphenyl-2(3H)-furanone (5a),<sup>29</sup> 3,5-diphenyl-3-(4-methylphenyl)-2(3H)-furanone (5b), 3,5-diphenyl-2-(4-methoxyphenyl)-2(3H)-furanone (5c), 3-(4-cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d) and 3-(4-chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e) were prepared by a general procedure outlined in Scheme I.3. The structures of 5b-e have been established on the basis of analytical results, spectral evidence and literature precedents.<sup>29</sup>

### I.3.2 Preparative Photochemistry and Product Identification.

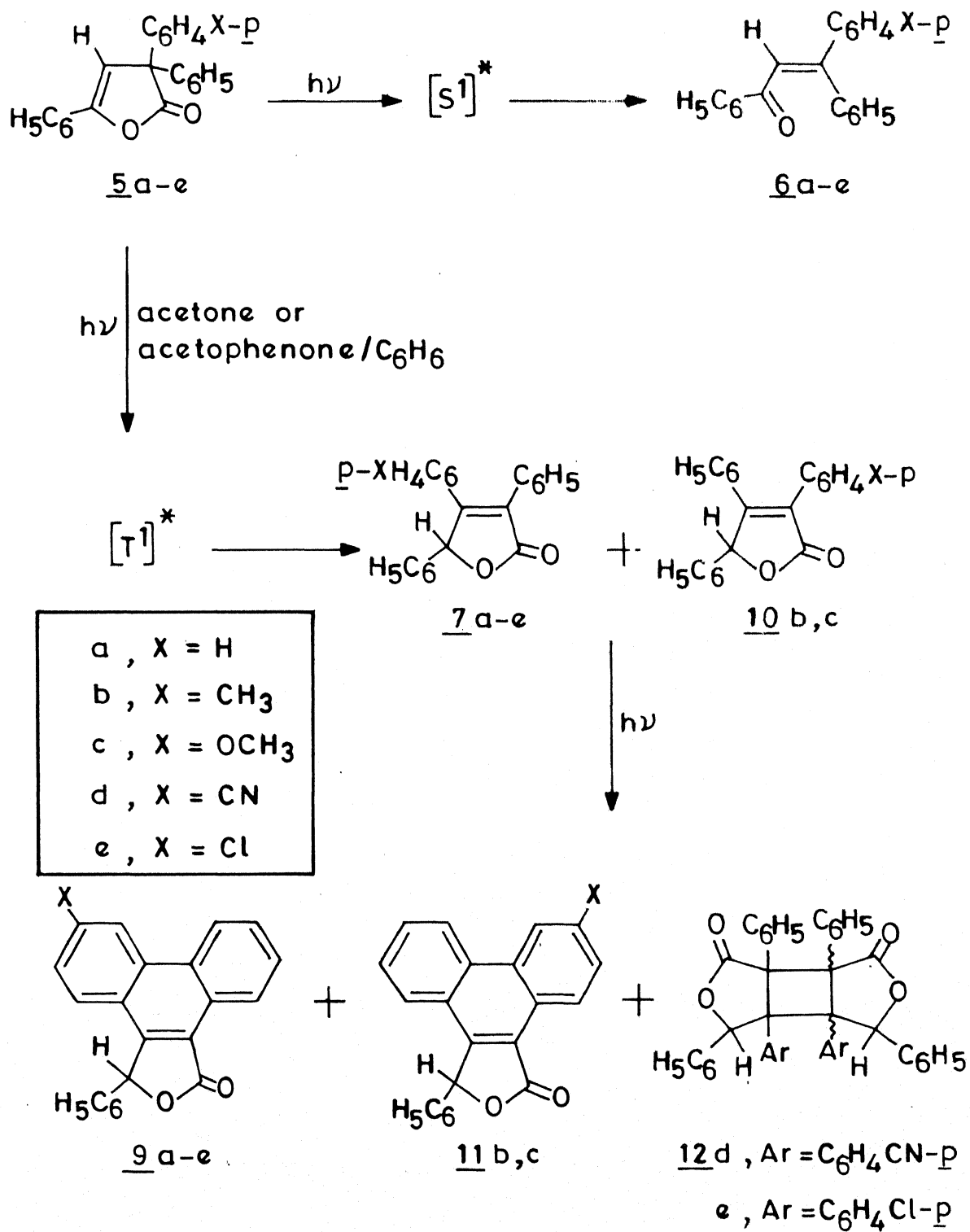
Direct irradiation of a solution of the 2(3H)-furanone 5a in



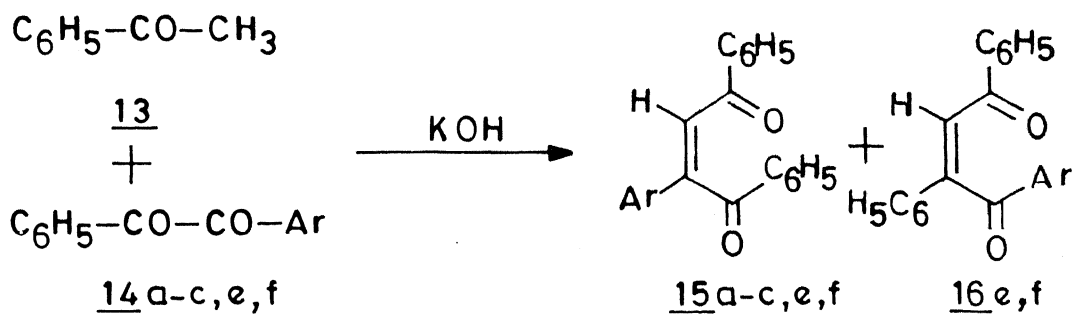
benzene and methanol gave the decarbonylated product 1,3,3-triphenylprop-2-en-1-one (6a)<sup>29</sup> in 87% and 66% yields, respectively. In contrast, when the irradiation was carried out in acetone, two products resulting from phenyl group migration from C-3 to C-4 position, viz. 3,4,5-triphenyl-2(5H)-furanone (7a, 15%)<sup>15</sup> and 3-phenylphenanthro[9,10-c]furan-1(3H)-one (9a, 65%) were obtained<sup>30</sup> (Scheme I.2). Similar results were obtained when the irradiation of 5a was carried out in benzene using acetophenone as sensitizer, under conditions wherein only the sensitizer absorbed all the light. On the other hand, when the sensitized irradiation was carried out in methanol, cis-5-methoxydihydro-3,4,5-triphenyl-2(3H)-furanone (23) was obtained in a 75% yield (Scheme I.5).

In order to gain a better understanding of the nature of the excited states in the photoreactions of 2(3H)-furanones, we have examined the reactions of different furanones 5b-e containing both electron withdrawing and donating substituents in the para position of one of the C-3 phenyl groups. Thus, irradiation of 5b in benzene and methanol gave 1,3-diphenyl-3-(4-methylphenyl)prop-2-en-1-one (6b), the decarbonylated product, in 84% and 60% yields, respectively, whereas irradiation in benzene, under acetophenone sensitization, gave a mixture of the rearranged 2(5H)-furanones 7b and 10b (30%) in a

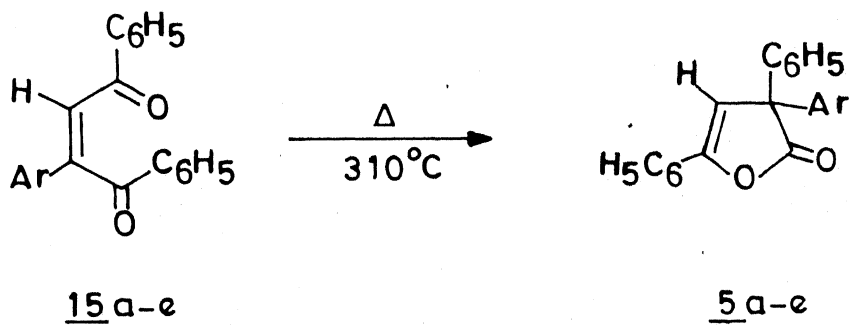
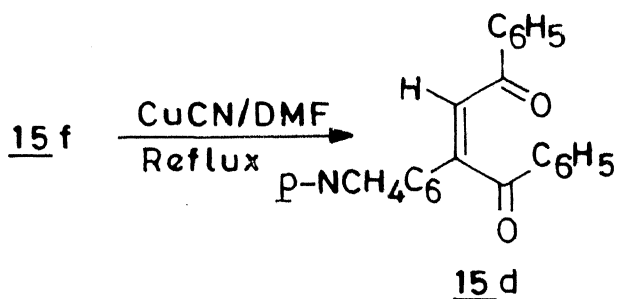
## Scheme 1.2



### Scheme 1.3



- a , Ar = C<sub>6</sub>H<sub>5</sub>  
 b , Ar = C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-p  
 c , Ar = C<sub>6</sub>H<sub>4</sub>OCH<sub>3</sub>-p  
 d , Ar = C<sub>6</sub>H<sub>4</sub>CN-p  
 e , Ar = C<sub>6</sub>H<sub>4</sub>Cl-p  
 f , Ar = C<sub>6</sub>H<sub>4</sub>Br-p



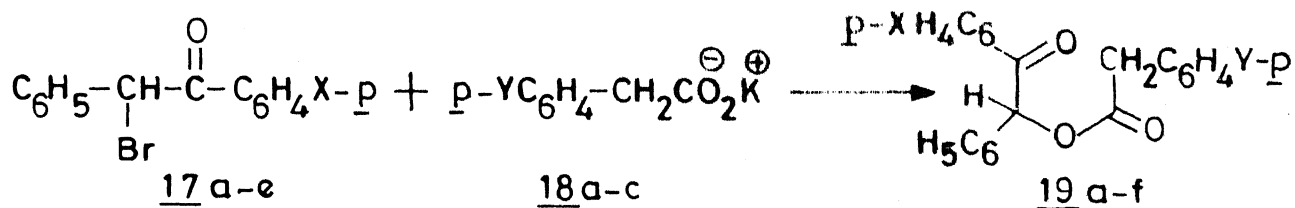
3:2 ratio, along with the corresponding phenanthrofuranones 9b and 11b (46%), in the same ratio (Scheme I.2). The structures of all the products were established on the basis of spectral data and also by comparison with authentic samples prepared through the route outlined in Scheme I.4.<sup>15,32</sup>

Mention may be made in this connection that <sup>1</sup>H NMR spectroscopy could be used as an efficient tool for determining the exact ratios of the photoproducts in these reactions.

Similarly, acetophenone sensitized irradiation of 5c gave a mixture of the 2(5H)-furanones 7c and 10c (29%) in a 2:3 ratio, along with the corresponding phenanthrofuranones 9c and 11c (49%), also in the same ratio. Direct irradiation of 5c in benzene and methanol, however, gave the decarbonylated product 6c in a 64% yield, in each case.

Likewise, the direct irradiation of 5d in benzene or methanol gave the decarbonylated product 6d in 85% and 87% yields, respectively. However, when the irradiation of 5d was carried out under acetophenone sensitization, only one of the two possible rearranged 2(5H)-furanones, namely 4-(4-cyanophenyl)-3,5-diphenyl-2(5H)-furanone (7d, 16%)<sup>15</sup> was obtained, along with the corresponding phenanthrofuranone 9d (18%) and a [2+2] photodimer 12d (40%) (Scheme I.2).

# Scheme 1.4



17a, X = H

b, X = CH<sub>3</sub>

c, X = OCH<sub>3</sub>

d, X = CN

e, X = Cl

18a, Y = H

b, Y = CH<sub>3</sub>

c, Y = OCH<sub>3</sub>

19a, X = CH<sub>3</sub>; Y = H

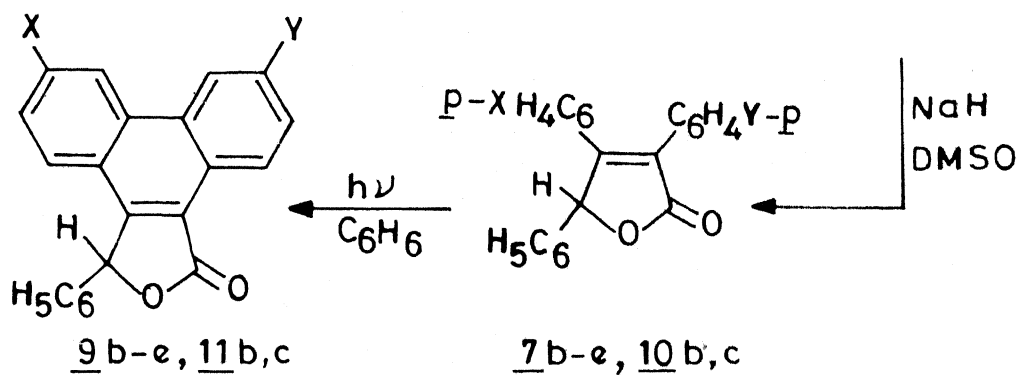
b, X = H; Y = CH<sub>3</sub>

c, X = OCH<sub>3</sub>; Y = H

d, X = H; Y = OCH<sub>3</sub>

e, X = CN; Y = H

f, X = Cl; Y = H



7 & 9b, X = CH<sub>3</sub>; Y = H

c, X = OCH<sub>3</sub>; Y = H

d, X = CN; Y = H

e, X = Cl; Y = H

10 & 11b, X = H; Y = CH<sub>3</sub>

c, X = H; Y = OCH<sub>3</sub>

The photolysis of 5e in benzene and methanol gave the decarbonylated product 6e in 82% and 76% yields, respectively, whereas under acetophenone sensitization, a mixture of 4-(4-chlorophenyl)-3,5-diphenyl-2(5H)-furanone (7e, 13%), the phenanthrofuranone 9e (13%) and the [2+2] photodimer 12e (53%) was obtained.

The structures of the photodimers 12d and 12e have been arrived at on the basis of analytical data, spectral evidence and literature precedents.<sup>15,17</sup> The <sup>1</sup>H NMR spectrum of 12d (Figure I.1), for example, showed a singlet at  $\delta$  5.07 (2 H), assigned to the protons at C-5 and C-5' positions. The aromatic protons have been observed as a complex multiplet, centred around  $\delta$  7.21 (28 H). Likewise, the <sup>1</sup>H NMR spectrum of 12e (Figure I.2) showed a singlet at  $\delta$  5.0 (2 H) and a multiplet centred around  $\delta$  7.16 (28 H, aromatic). As is evident from Figure I.2, the singlet at  $\delta$  5.0 is resolved into two peaks upon expansion, indicating that the two protons are not exactly equivalent. This agrees very well with the head-to-head structure rather than a head-to-tail structure for the dimer. It may be pointed out here that these photodimers were formed in greater amounts in concentrated solutions ( $\sim 10^{-2}$  M or more), whereas in dilute solutions ( $\sim 10^{-3}$  M), dimer formation could be suppressed to a

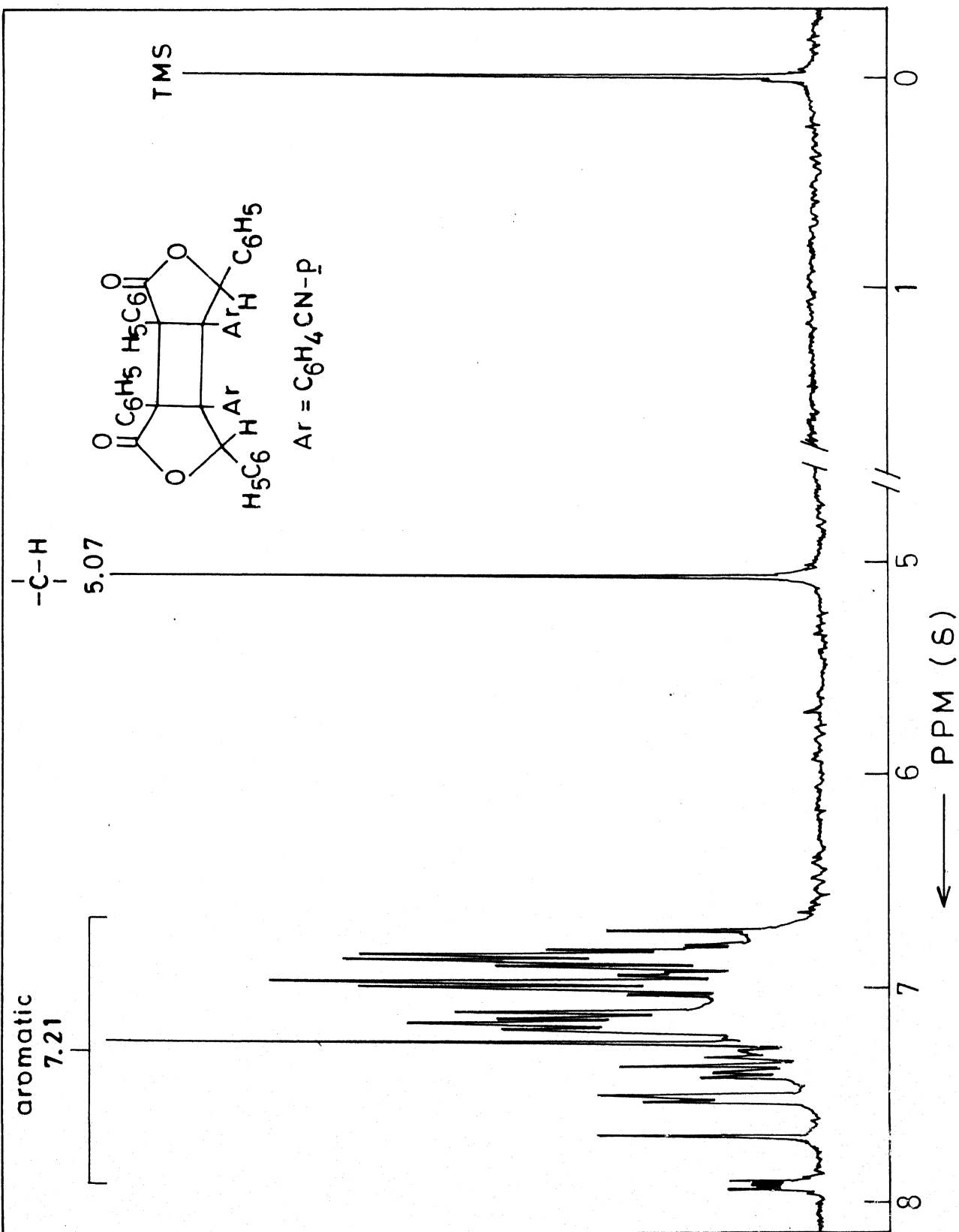


Figure 1,1 <sup>1</sup>H NMR spectrum (270 MHz) of 12d.

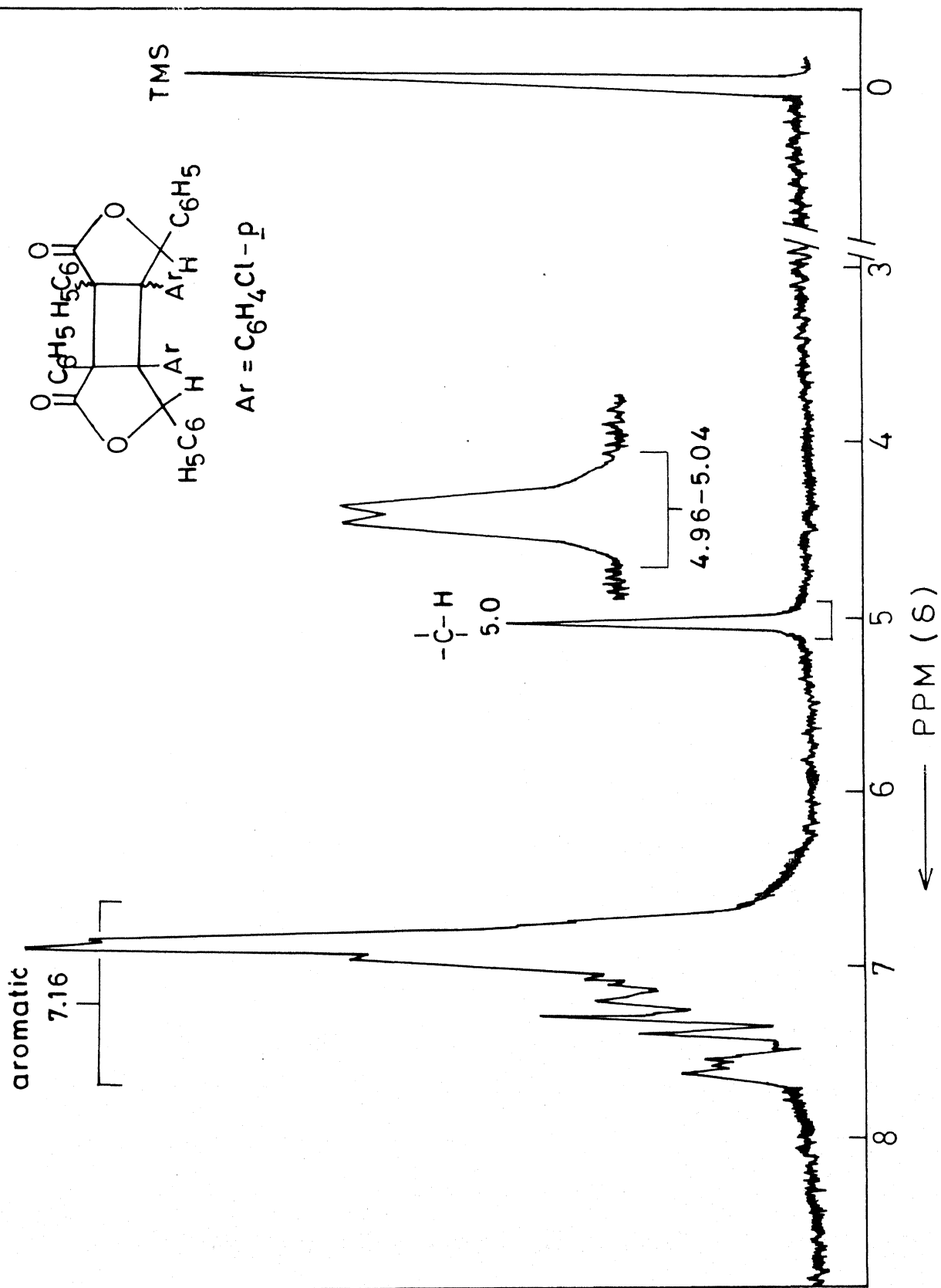


Figure 1.2  $^1\text{H}$  NMR spectrum (90 MHz) of 12e.



reasonable extent and hence the photorearrangement products could be observed under these conditions.

**I.3.3 Laser Flash Photolysis Studies.**<sup>33</sup> In order to shed light on the precursors and intermediates that lead to the photoproducts observed under steady-state photolysis (vide supra), the 2(3H)-furanones 5a-e and the 2(5H)-furanones 7a,b,d and 10b,c were subjected to laser flash photolysis studies. To generate the intermediates, both direct excitation and triplet sensitization were employed. Attempts were also made to observe the transients in terms of their absorption at 250-750 nm over 100 ns - 100  $\mu$ s, following the nanosecond laser pulse excitation.

**(a) Direct Excitation of 2(3H)- and 2(5H)-Furanones.**

Upon 248 nm laser pulse excitation, methanolic solutions of 2(3H)-furanones 5a-e give rise to photoproducts, characterized by absorption maxima ( $\lambda_{\max}^P$ ) at 300-335 nm and showing no sign of decay over the longest time scale ( $\sim 100 \mu$ s) used in our experiments. A representative case with 5d as the substrate is illustrated in Figure I.3. The yields, as well as the decay behaviour of the 'permanent' photoproducts are unaffected by the presence of oxygen (2.1 mM) in the solution. The photoproduct absorption maxima ( $\lambda_{\max}^P$ ), listed in Table I.1 show a substituent effect similar to that of the ground state absorption maxima of the photodecarbonylation products, 6a-e.

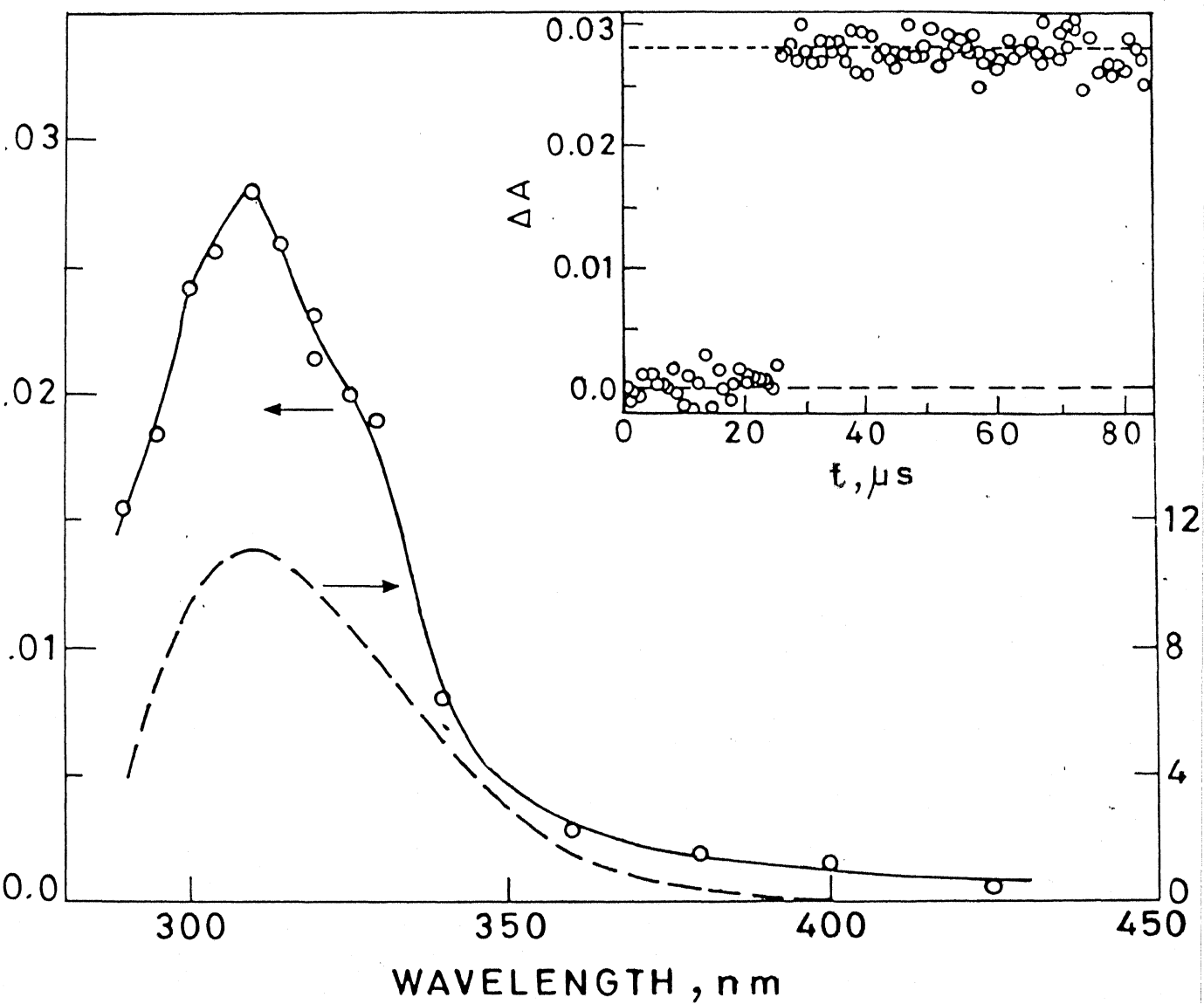


Figure I.3 Absorbance changes at 3  $\mu$ s following laser flash photolysis of 5d in methanol. The broken curve is the difference absorption spectrum of 6d and 5d in methanol. The inset shows a kinetic trace at 310 nm for this system.

Table I.1 Photoproduct Absorption Maxima and Yields in  
Methanol ( $\lambda_{\text{ex}} = 248 \text{ nm}$ ). <sup>a</sup> Temperature : 295 K

Substrate	$\lambda_{\text{max}}^{\text{P}}, \text{ nm } ^{\text{b}}$	$\phi_{\text{P}}$
<u>5a</u>	300	0.32
<u>5b</u>	330	0.27
<u>5c</u>	330	0.20
<u>5d</u>	300	0.22
<u>5e</u>	310	0.30
<u>7a</u>	325, 490	0.61 (0.42) <sup>c</sup>
<u>7b</u>	330, 490	0.53 (0.36) <sup>c</sup>
<u>7d</u>	335, 500	0.45 (0.34) <sup>c</sup>
<u>10b</u>	325, 490	0.61 (0.34) <sup>c</sup>
<u>10c</u>	330, 490	0.69 (0.38) <sup>c</sup>

<sup>a</sup> Except for the  $\phi_{\text{P}}$  data in paranthesis. These values are obtained in benzene with  $\lambda_{\text{ex}} = 308 \text{ nm}$ .

<sup>b</sup>  $\pm 5 \text{ nm}$

<sup>c</sup> Calculated with the assumption that  $\epsilon_{\text{max}}^{\text{P}}$  of each of 4a,4b-dihydrophenanthrenes at 490-500 nm is  $6.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  (see text).

For example,  $\lambda_{\max}^P$  (330-335 nm) is found to be most red-shifted in the case of 5b and 5c; the decarbonylation products, 6b and 6c obtained from these two substrates, respectively, have  $\lambda_{\max}$  at 334-336 nm, compared to 296-312 nm for 6a,d,e (in methanol). Based on spectral similarity with the photoproducts 6a-e, permanent nature, and insensitivity towards oxygen, we assign the species observed under direct laser excitation of 5a-e as the  $\alpha,\beta$ -unsaturated ketones 6a-e. This assignment is further corroborated by the fact that the observed spectrum agrees very well with the difference absorption spectrum of the  $\alpha,\beta$ -unsaturated ketone and the parent furanone (Figure I.3). Thus, in our time resolved measurements, the two-bond cleavage leading to photoextrusion of carbon monoxide appears as a concerted process occurring within nanoseconds of laser photoexcitation. In other words, we do not observe the biradicals, that could be formed by the cleavage of one of the bonds to the carbonyl group in the 2(3H)-furanone, which is predicted to be an intermediate in decarboxylation reactions by earlier workers.<sup>7</sup>

The 308 or 248 nm laser flash photolysis of 2(5H)-furanones 7a,b,d and 10b,c in benzene or methanol results in the formation of long-lived photoproducts displaying dual absorption maxima at 325-335 and 490-500 nm. The photoproduct

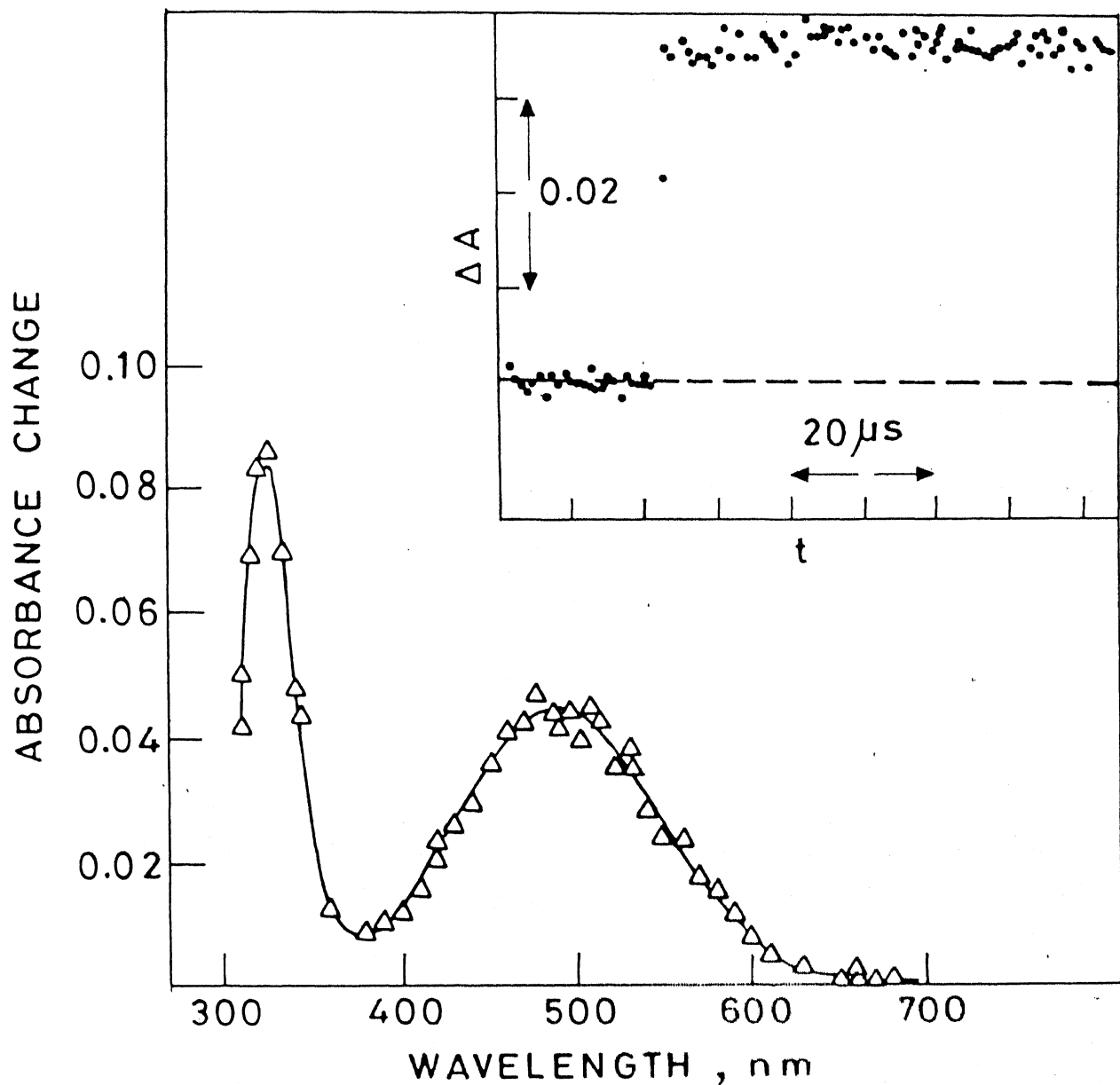


Figure I.4 Transient absorption spectrum at 3.5  $\mu\text{s}$  following 248 nm laser flash photolysis of 10b in methanol. Inset shows a typical kinetic trace for this system at 495 nm.

absorption spectrum with 10b as the substrate in methanol is shown in Figure I.4. The long-lived nature of the photo-products is evident from the fact that they undergo little or no decay ( $< 5\%$ ) on the longest time scale ( $\sim 100 \mu\text{s}$ ). Considering the fact that phenanthrene derivatives 9a-e and 11b,c are isolated in high yields in the course of exhaustive photolysis of 5a-e under triplet sensitization as well as under direct photolysis of 7b-e and 10b,c (vide supra), it seems plausible that the observed 330/490 nm species are 4a,4b-dihydrophenanthrene derivatives, formed by cyclization involving the C-3 and C-4 phenyl groups present in the 2(5H)-furanones. This assignment is supported by the similarity of the absorption spectra with those of 4a,4b-dihydrophenanthrenes produced from cis-stilbene and diphenylcyclopentene under steady-state photolysis at subambient temperatures.<sup>34</sup> Also, in an earlier study from this laboratory, spectrally and kinetically similar photoproducts were observed in the laser flash photolysis of 4,5-diphenyl-substituted 2(3H)-furanones.<sup>30</sup>

Attempts were also made to calculate the photoproduct yields ( $\phi_p$ ) from 2(3H)- and 2(5H)-furanones under direct laser excitation. Triplet formation of naphthalene (in cyclohexane,  $\lambda_{\text{max}}^T = 414 \text{ nm}$ ,  $\epsilon_{\text{max}}^T = 24.5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\phi_T = 0.75$ )<sup>35</sup> and benzophenone (in benzene  $\lambda_{\text{max}}^T = 532 \text{ nm}$ ,  $\epsilon_{\text{max}}^T = 7.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\phi_T = 1.0$ )<sup>35</sup> were used for actinometry for solutions

in methanol ( $\lambda_{\text{ex}} = 248 \text{ nm}$ ) and in benzene ( $\lambda_{\text{ex}} = 308 \text{ nm}$ ), respectively. To calculate  $\phi_P$ , the following equation was used,

$$\phi_P = \phi_T \cdot \frac{\Delta A_P}{\Delta A_T} \cdot \frac{\epsilon_T^R}{\epsilon_P}$$

where  $A$ 's represent end-of-pulse absorbance changes,  $\epsilon$ 's are extinction coefficients at the monitoring wavelengths, and R and P designate reference (naphthalene or benzophenone) and photoproduct, respectively. For decarbonylation products i.e.,  $\alpha,\beta$ -unsaturated ketones 6a-e,  $\epsilon_P$ 's were measured for the isolated compounds. For dihydrophenanthrenes,  $\epsilon_P$ 's at 490-500 nm were assumed to be the same as that reported for 4a,4b-dihydrophenanthrene from cis-stilbene ( $6.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ )<sup>34</sup> in 2:1 methylcyclohexane and isohexane at 263 K. The  $\lambda_{\text{max}}^P$  and  $\phi_P$  data for the photoproducts from the different furanones under study are given in Table I.1. In spite of large uncertainties in  $\epsilon_P$ 's and hence  $\phi_P$ 's (Table I.1), both photodecarbonylation and photocyclization can be considered as efficient photoreactions of 2(3H)- and 2(5H)-furanones, respectively.

(b) Triplet Sensitization. The photoreaction of major interest in this investigation is the triplet mediated rearrangement of 2(3H)-furanones. Hence, the properties of the triplet of 2(3H)-furanones 5a-e are mechanistically relevant. The 2(3H)-furanones do not have significant

absorption above 320 nm. Thus, they could be examined as acceptors of energy from benzophenone and acetophenone triplets produced by laser excitation of the ketones at 337 or 355 nm, without interference from direct excitation of the furanones. It is worth mentioning here that the furanones under consideration contain styrene moieties constrained into planar geometries. Since their triplet energies should not be very different from the spectroscopic triplet energy of styrene ( $E_T = 62 \text{ kcal mol}^{-1}$ ),<sup>36</sup> these substrates should quench the aromatic ketone triplets via exothermic energy transfer.

Upon 337 or 355 nm laser excitation of benzophenone (0.04–0.06 M) or acetophenone ( $\sim 0.1 \text{ M}$ ) in the presence of 5–25 mM 5a–d in benzene, we observe short-lived transients with absorption maxima at 335–340 nm. Two representative examples are given in Figure I.5. The transients decay by clean first order kinetics leading to weak residual absorptions with maxima  $< 320 \text{ nm}$  (see kinetic traces in Figure I.5). Based on their quenching behaviour towards oxygen, 2,5-dimethyl-2,4-hexadiene and ferrocene, we assign the 335–340 nm transients as the triplets of the 2(3H)-furanones. The rate constants for the quenching of the triplet of 5a by the aforementioned quenchers in benzene are  $1.6 \times 10^9$ ,  $9.8 \times 10^8$ , and  $5.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.



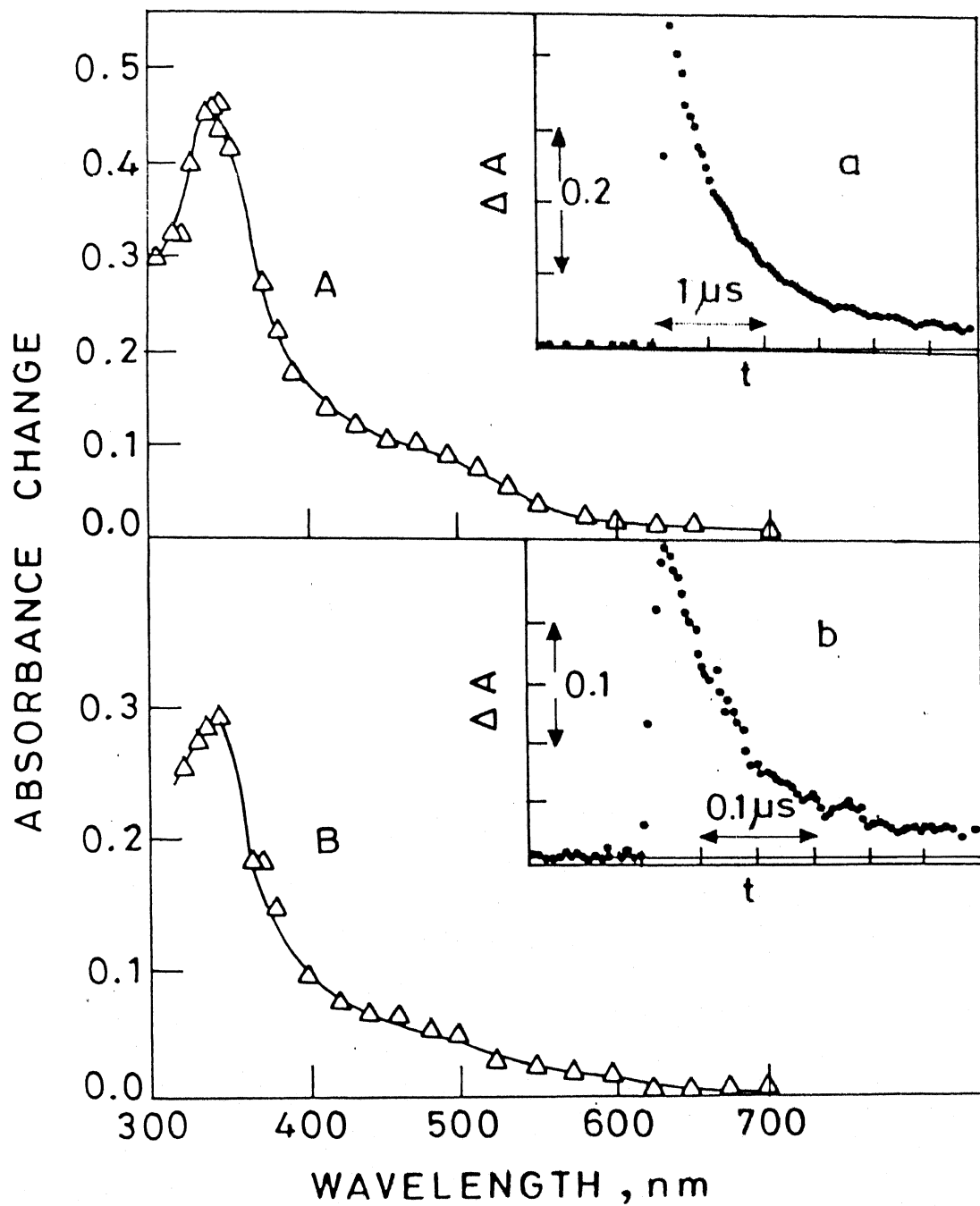


Figure I.5 Transient absorption spectra (A) at 0.5  $\mu\text{s}$  following 355 nm laser excitation of benzophenone in the presence of 5b and (B) at 0.04  $\mu\text{s}$  following 355 nm laser excitation of acetophenone in the presence of 5d. Solvent benzene. Insets: kinetic traces showing the triplet decay at 340 nm.

The triplet decay lifetimes were measured in benzene as a function of the ground-state concentrations in the range 4-25 mM. The self-quenching rate constants were negligible ( $< 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ). The triplet lifetimes ( $\tau_T$ ) in benzene obtained by extrapolation to zero concentrations are all in the submicrosecond time domain (Table I.2). In Table I.2 are also given the triplet lifetimes in methanol measured under sensitization by p-methoxyacetophenone at ca. 10 mM substrate concentration. It can be noted that except for 5d,  $\tau_T$ 's in methanol are slightly longer than in benzene. The oxygen quenching rate constants ( $k_{q,O_2}^T$ , Table I.2) are all in the vicinity of  $1/9 k_{diff}$ , suggesting energy transfer to be important in the interaction of the styrene-like, but planar, triplets with oxygen.

The triplets of the 2(5H)-furanones also were generated in benzene under energy transfer sensitization by benzophenone triplet ( $\lambda_{ex} = 355 \text{ nm}$ ). These are characterized by broad and featureless absorption spectra with maxima at 360-380 nm (except for 10c, for which  $\lambda_{max}^T$  is red-shifted to 440 nm). The triplet lifetimes measured at 1 mM substrate concentrations are in the range 4-10  $\mu\text{s}$ . These transients are not produced at all under direct photolysis of the 2(5H)-furanones. Also, no long-lived residual absorptions at 490-500 nm, attributable to 4a,4b-dihydrophenanthrenes,

Table I.2 Spectral and Kinetic Properties of 2(3H)-Furanone Triplets in Benzene. Temperature: 295 K.

Substrate	$\lambda_{\max}^T$ , nm <u>a</u>	$\tau_T$ , $\mu$ s <u>b,c</u>	$k_{q,O_2}^T$ <u>b</u> $\cdot 10^9$ M <sup>-1</sup> s <sup>-1</sup>
<u>5a</u>	335	0.92 (1.03)	1.6 (2.1)
<u>5b</u>	335	0.75 (0.99)	1.8 (2.0)
<u>5c</u>	340	0.86 (1.02)	1.5 (1.9)
<u>5d</u>	335	0.061 (0.036)	1.6
<u>5e</u>	340	0.68 (0.70)	1.7 (1.8)

a  $\pm$  5 nm

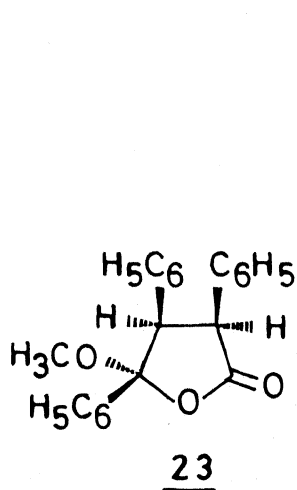
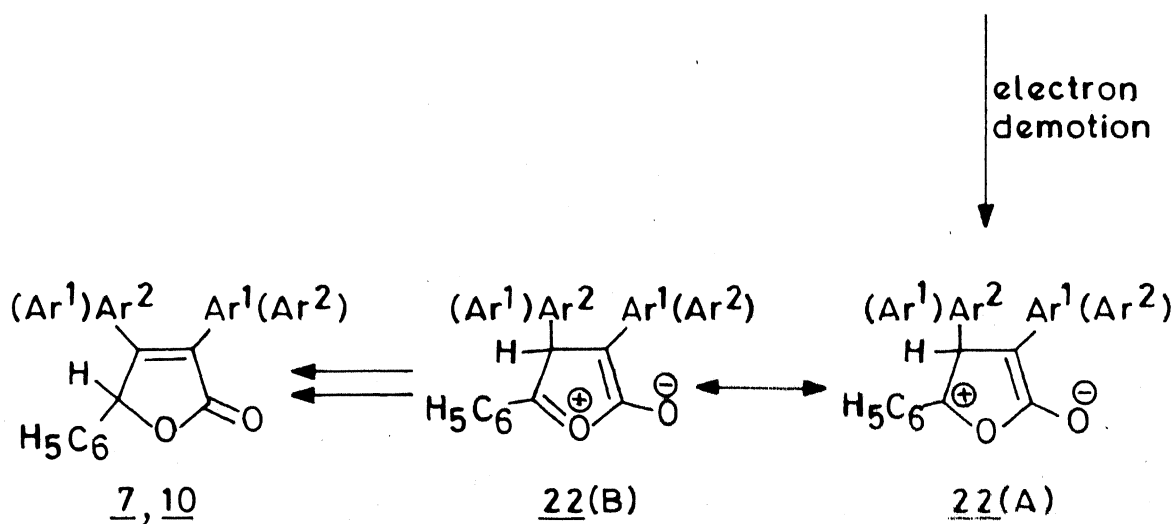
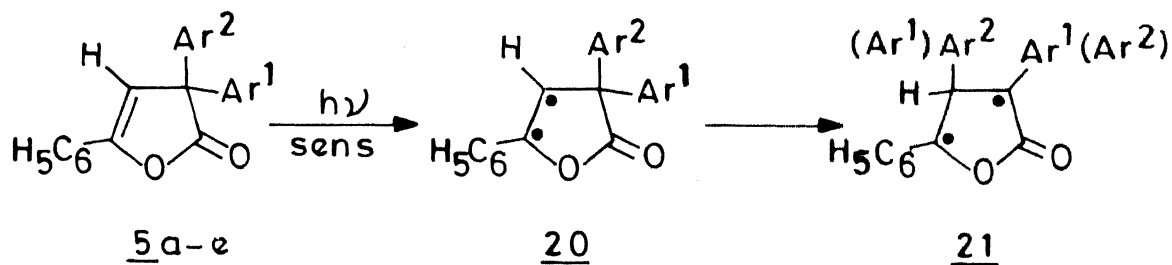
b  $\pm$  15%; the data in the parentheses are in methanol.

c Triplet lifetimes in benzene were obtained from extrapolation to zero substrate concentrations; those in methanol were measured at  $\sim$  10 mM substrate concentrations.

are observed following the decay of the 2(5H)-furanone triplets. These results establish that the photocyclization reaction leading to dihydrophenanthrenes is singlet mediated and that its occurrence in the course of the sensitized irradiation of 2(3H)-furanones is due to direct light absorption by 2(5H)-furanones (initial products) at a later stage of the photolysis. As expected, the triplet lifetimes (4-10  $\mu$ s) of the 3,4,5-triaryl-2(5H)-furanones under consideration are significantly longer than those (< 1 ns) estimated for photoreactive 3,5,5-triaryl-2(5H)-furanones studied by Padwa and co-workers.<sup>15</sup> The latter 2(5H)-furanones undergo C-5 to C-4 aryl group migration in the triplet state, the lifetime of which has been measured by piperylene quenching of the reaction under steady-state condition.<sup>15</sup>

**I.3.4 Discussion.** The photochemical rearrangement of the 2(3H)-furanones 5a-e to give the corresponding 2(5H)-furanones 7a-e and 10b,c and the subsequent formation of the corresponding phenanthrofurones 9a-e and 11b,c, can be explained in terms of the pathways shown in Scheme I.5 involving the triplet excited state. In the triplet excited state, which can also be visualized in terms of a diradical structure (20), one of the C-3 aryl groups migrates through a bridged transition state to give the rearranged diradical intermediate 21. Electron demotion in 21 will lead to a

## Scheme 1.5



- a ,  $\text{Ar}^1 = \text{Ar}^2 = \text{C}_6\text{H}_5$

b ,  $\text{Ar}^1 = \text{C}_6\text{H}_5$  ;  $\text{Ar}^2 = \text{p-CH}_3\text{C}_6\text{H}_4$

c ,  $\text{Ar}^1 = \text{C}_6\text{H}_5$  ;  $\text{Ar}^2 = \text{p-CH}_3\text{OC}_6\text{H}_4$

d ,  $\text{Ar}^1 = \text{C}_6\text{H}_5$  ;  $\text{Ar}^2 = \text{p-CNC}_6\text{H}_4$

e ,  $\text{Ar}^1 = \text{C}_6\text{H}_5$  ;  $\text{Ar}^2 = \text{p-ClC}_6\text{H}_4$

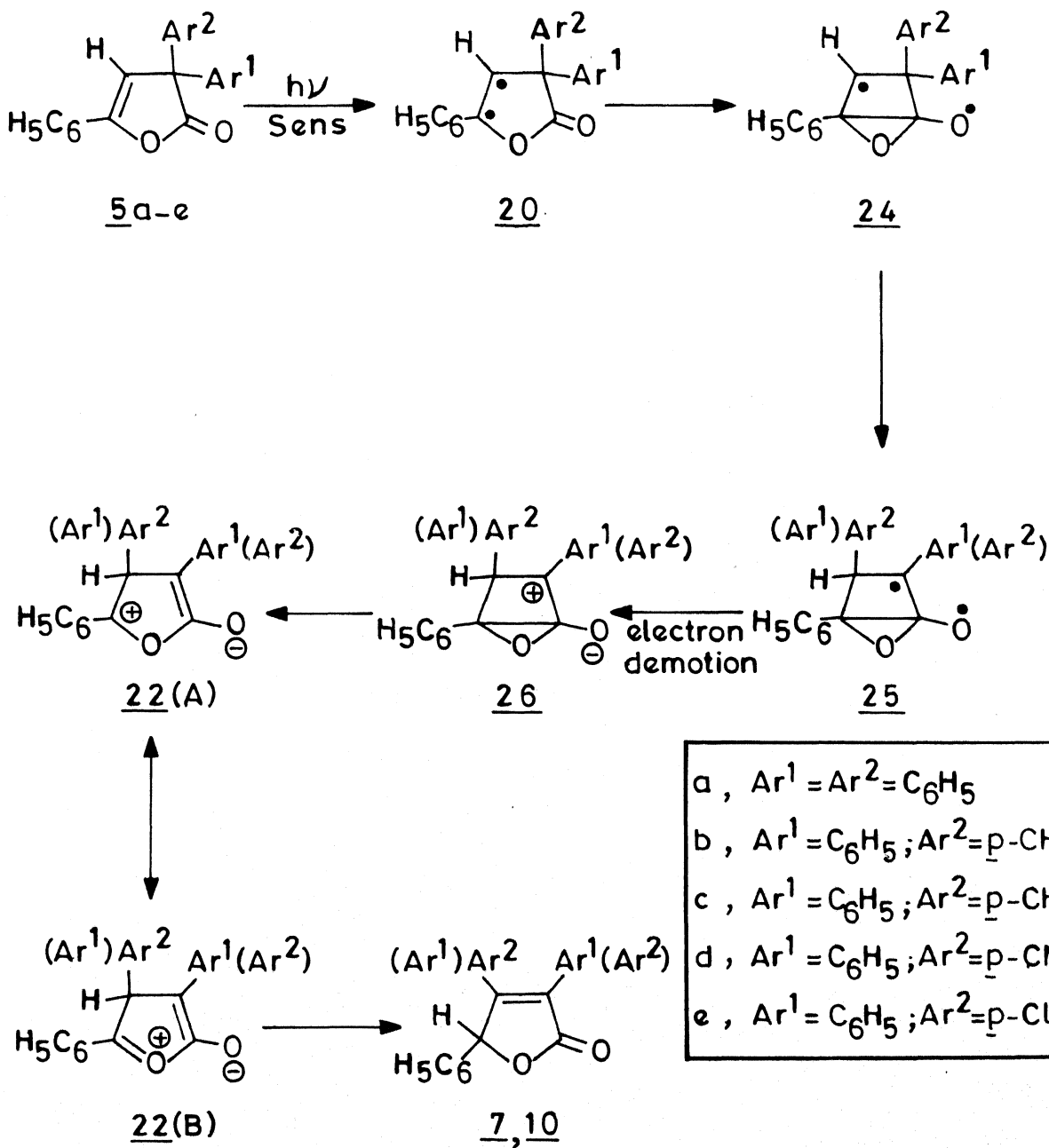
zwitterionic intermediate described by structures 22(A) and 22(B). In the presence of methanol, for example, the zwitterionic intermediate is trapped to give the methanol adduct 23. In the absence of any hydroxylic solvents, the zwitterionic intermediate undergoes prototropic shifts to give the rearranged 2(5H)-furanones 7a-e and 10b,c. These furanones, in turn, absorb light and undergo further photocyclization leading to dihydrophenanthrofuranones; the latter give the phenanthrofuranones 9a-e and 11b,c through air-oxidation (under the conditions of workup). Alternatively, these 2(5H)-furanones can undergo [2+2] photocycloaddition, leading to the dimeric products 12d,e.

The observed migratory aptitudes of the para substituted phenyl groups at C-3 position are in support of the pathways outlined in Scheme I.5. In the case of 5,5-diaryl-2(5H)-furanones in benzene, Padwa et al.<sup>15</sup> have observed that p-anisyl or p-cyanophenyl groups migrate in preference to a phenyl group. This has been attributed to the lower free energy of the bridged transition state in which the free valence is stabilized by the para substituent of the migrating aryl group. For the substrates under study, we have observed complete migration of p-chlorophenyl and p-cyanophenyl groups (against phenyl) and a preference of

phenyl group migration over p-anisyl group. This latter trend was also observed by Padwa et al.<sup>15</sup> in the case of 2(5H)-furanones, when the irradiations were carried out in alcoholic solvents. This has been attributed to the stabilization of the positive charge developed at the C-5 centre of the furanones by the substituents on the nonmigrating aryl group. Our results with 2(3H)-furanones in benzene are compatible with the view that the rearrangement proceeds directly from the triplet state and not from any subsequent ground state zwitterionic intermediates. The preferential migration of p-chlorophenyl and p-cyanophenyl groups over phenyl group migration in the 2(3H)-furanones under investigation suggests that the C-4 centre (migration terminus) in the excited state of these furanones has odd electron character. The high preference of p-cyanophenyl group migration agrees well with that observed in analogous triplet-mediated photorearrangements of cyclohexenones,<sup>37</sup> naphthalenones<sup>38</sup> and 2(5H)-furanones.<sup>15</sup>

The relative reluctance of p-anisyl group to migrate is difficult to explain in terms of the diradical structures shown in Scheme I.5. It suggests that in the course of aryl group migration, the electron density at C-3 is decreased and that the positive centre at this position is stabilized

# Scheme 1.6





by the p-anisyl group. Although formally nonconjugated, the styryl and carbonyl groups in 2(3H)-furanones are expected to interact strongly through favourable  $\pi$  orbital overlap. That the latter does occur is evident from the fact that the diene quenching of the 2(3H)-furanone triplets is far less than diffusion controlled ( $k_q^T < 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), suggesting a considerable lowering of  $E_T$  (relative to that of styrene,  $E_T = 62 \text{ kcal mol}^{-1}$ ). In the light of the interaction of the styrene and carbonyl moieties, one can invoke valence-bond structures 24 and 25, arising from the diradical 20 (Scheme I.6). Electron demotion in 25 leads to the zwitterionic intermediate 26 in which the C-3 carbon centre bears a positive charge. The zwitterionic intermediate 26 would be better stabilized by a nonmigrating p-anisyl group at C-3 than a nonmigrating phenyl group. The same mechanism could also be contributing towards the observed trend in migration in the case of 5d and 5e, where a nonmigrating phenyl group stabilizes the zwitterionic intermediate 26 better than p-chlorophenyl or p-cyanophenyl groups.

The short lifetimes of the triplets of 2(3H)-furanones 5a-e are indicative of their photoreactive nature. These lifetimes (Table I.2) are intermediate between those of the

triplets of styrene (20-90 ns in methanol) which are recognized to exist in orthogonal configurations<sup>39</sup> and those of the triplets of 3,4,5-triaryl-substituted 2(3H)-furanones<sup>30</sup> (8-12  $\mu$ s) which cannot undergo the sensitized rearrangement. One can note that furanone 5d has significantly shorter triplet lifetime compared to its analogues (Table I.2). This probably reflects a higher propensity of the *p*-cyanophenyl group to migrate, rather than an enhanced inter-system crossing ( $T \rightarrow S_0$ ) in this system. If the latter were true, the sensitized photoreactivity of 5d would be relatively sluggish. Steady-state photolysis studies show the opposite to be true.

The triplet lifetime data allow us to make direct estimates of the rates of intramolecular aryl group migration in the triplets of 3,3,5-triaryl-2(3H)-furanones. Since the observed  $\tau_T$ 's (Table I.2) are more than 10 times shorter than those of related 2(3H)-furanones in which the sensitized photorearrangement cannot occur,<sup>30</sup> it is reasonable to assume that the triplet decay of the photoreactive 2(3H)-furanones 5a-e is predominantly controlled by the aryl group migration (that is, the quantum yield,  $\Phi_{PR}$  of the photorearrangement is close to unity). This should be particularly true in the case of 5d, where  $\tau_T$  is unusually short

(Table I.2). Based on  $\phi_{PR} = 1$ , the rate constants for triplet-state migration of phenyl group in 5a and of p-cyanophenyl group in 5d are calculated to be  $5.4 \times 10^5$  and  $1.6 \times 10^7 \text{ s}^{-1}$ , respectively (in benzene). These rates are substantially smaller than the migrating rates of the same aryl groups ( $1.8 \times 10^9$  and  $9 \times 10^9 \text{ s}^{-1}$  in benzene) in 3,5,5-triaryl-2(5H)-furanone triplets, estimated by piperylene quenching studies.<sup>15</sup> Also, note that  $\tau_T$  of 5c is nearly the same as that of 5a (Table I.2), suggesting that the p-anisyl group as a migrant is far inferior to the p-cyanophenyl group and that its ability to help in the migration of the geminal phenyl group is only marginal.

#### I.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on either Perkin-Elmer Model 377 or Model 580 infrared spectrometers. The electronic spectra were recorded on Beckman DB, Cary 17D, or Cary 219 spectrophotometers. The NMR traces were recorded on Varian A-60, EM-390 or Bruker 270 MHz spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer or a Varian Mat CH7 mass

spectrometer at 70 eV. Irradiations were carried out in Srinivasan-Griffin-Rayonet photochemical reactor (RPR 2537, 3000 or 3500 Å) or using a Hanovia 450-W medium pressure mercury lamp in a quartz jacketed immersion well.

I.4.1 Starting Materials. The furanone 5a,<sup>29</sup> mp 120-121 °C was prepared by a reported procedure. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

I.4.2 Preparation of 2(3H)-Furanones 5b-e. A general procedure for the preparation of furanones 5b-e involved heating of the appropriate but-2-en-1,4-diones 15b-e around 300 °C in a sealed tube for 1-1.5 h and workup of the mixture by extraction with methylene chloride, chromatographing over silica gel (elution with mixtures of benzene and petroleum ether), followed by recrystallization from suitable solvents.

The but-2-en-1,4-diones 15b,c were prepared through the condensation of the appropriate benzil derivatives 14b,c with acetophenone in the presence of potassium hydroxide in ethanol. In a typical experiment, a mixture of 25 mmol of the benzil derivative, 27 mmol of acetophenone

and 1.0 g of powdered potassium hydroxide in 30 mL of ethanol was stirred around 50-60 °C for 15 minutes and later kept in a refrigerator for a couple of days. The solid product that separated out was filtered and recrystallized from suitable solvents.

1,4-Diphenyl-2-(4-methylphenyl)but-2-en-1,4-dione (15b).

15b was obtained in a 63% yield, mp 145-146 °C, after recrystallization from ethanol.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 2850 (CH), 1660, 1655 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  2.25 (s, 3 H, methyl) and 7.25 (m, 15 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 84.26; H, 5.16.

3,5-Diphenyl-3(4-methylphenyl)-2(3H)-furanone (5b). 5b

was obtained in a 60% yield, mp 109-110 °C, after recrystallization from ethanol.

IR spectrum  $\nu_{\max}$  (KBr): 3120, 3040, 3025, 2910 (CH), 1780 (C=O), 1660 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 248 nm ( $\epsilon$ , 6,400), 270 (12,800).

$^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  2.33 (s, 3 H, methyl), 6.3 (s, 1 H, vinylic) and 7.4 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 84.60; H, 5.12.

1,4-Diphenyl-2-(4-methoxyphenyl)but-2-en-1,4-dione (15c). 15c was obtained in a 51% yield, mp 104-105  $^\circ\text{C}$ , after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3060, 2960, 2820 (CH), 1655, 1640 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  3.75 (s, 3 H, methoxy) and 7.4 (m, 15 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_3$ : C, 80.70; H, 5.26. Found: C, 80.56; H, 5.10.

3,5-Diphenyl-3-(4-methoxyphenyl)-2(3H)-furanone (5c). 5c was prepared in a 50% yield, mp 92-93  $^\circ\text{C}$ , after recrystallization from ethanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3120, 3060, 2840 (CH), 1780 (C=O) and 1610 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 247 nm ( $\epsilon$ , 7,300), 271 (12,400).

$^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  3.75 (s, 3 H, methoxy), 6.3 (s, 1 H, vinylic) and 7.15 (m, 14 H, aromatic).

Anal. Calcd for  $C_{23}H_{18}O_3$ : C, 80.70; H, 5.26. Found: C, 80.60; H, 5.08.

2-(4-Cyanophenyl)-1,4-diphenylbut-2-en-1,4-dione (15d).

A mixture of p-bromobenzil (5.5 g, 20 mmol), acetophenone (2.6 g, 21 mmol) and potassium hydroxide (0.75 g) in ethanol (40 mL) was stirred around 40 °C for 30 minutes and worked up in the usual manner to give a mixture (4.0 g, 53%, mp 90 °C) of 2-(4-bromophenyl)-1,4-diphenylbut-2-en-1,4-dione (15f) (major) and 1-(4-bromophenyl)-2,4-diphenylbut-2-en-1,4-dione (16f) (minor). This mixture (3.91 g, 10 mmol) was combined with cuprous cyanide (2.68 g, 30 mmol) and stirred in refluxing dimethylformamide (DMF) for 5 h. The reaction mixture was poured into aqueous sodium cyanide solution (5%, 25 mL) and extracted with benzene. Removal of the solvent from the benzene layer gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (4:1) of benzene and petroleum ether gave 300 mg (9%) of 1-(4-cyanophenyl)-2,4-diphenylbut-2-en-1,4-dione (16d), mp 142-143 °C (minor product). Further elution of the column with benzene gave 1.8 g (53%) of 2-(4-cyanophenyl)-1,4-diphenylbut-2-en-1,4-dione (15d), mp 178-179 °C, after recrystallization from benzene.

IR spectrum  $\nu_{\max}$  (KBr): 3100, 3070 (CH), 2240 (C≡N), 1675, 1660 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  7.6 (m, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{NO}_2$ : C, 81.89; H, 4.45; N, 4.15.

Found: C, 82.01; H, 4.80; N, 4.20.

3-(4-Cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d). 5d

was obtained in a 50% yield, mp 114-115  $^\circ\text{C}$ , after recrystallization from a mixture (1:1) of carbon tetrachloride and petroleum ether.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3100, 3050, 3030 (CH), 2215 ( $\text{C}\equiv\text{N}$ ), 1780 ( $\text{C}=\text{O}$ ), 1650 and 1600 ( $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 240 nm ( $\epsilon$ , 22,700), 270 (21,600).

$^1\text{H}$  NMR spectrum ( $\text{CCl}_4$ ):  $\delta$  6.2 (s, 1 H, vinylic) and 7.2 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{NO}_2$ : C, 81.89; H, 4.45; N, 4.15.

Found: C, 82.19; H, 4.95; N, 4.37.

3-(4-Chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e). A

mixture of p-chlorobenzil<sup>40</sup> (4.89 g, 20 mmol), acetophenone (2.4 g, 20 mmol) and potassium hydroxide (2.0 g) in ethanol (30 mL) was stirred at room temperature ( $\sim 30^\circ\text{C}$ ) for 2 h and worked up in the usual manner to give a mixture (4.0 g, 69%, mp 82-85  $^\circ\text{C}$ ) of 2-(4-chlorophenyl)-1,4-diphenylbut-2-en-1,4-dione (15e) and 1-(4-chlorophenyl)-2,4-diphenylbut-2-en-



1,4-dione (16e). The mixture of 1,4-diones (1.73 g, 5 mmol) was heated at 270 °C for 5 h and worked up as in the earlier cases to give 1.0 g (57%) of 5e, mp 98-99 °C, after recrystallization from ethanol.

IR spectrum  $\nu_{\max}$  (KBr): 3080, 3060, 3030 (CH), 1795 (C=O), 1650 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 218 nm ( $\epsilon$ , 31,400), 230 (22,400), 270 (18,600), 294 (sh, 5,800).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  6.36 (s, 1 H vinylic) and 7.66 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{ClO}_2$ : C, 76.30; H, 3.78. Found: C, 76.56; H, 3.64.

#### I.4.3 Photolysis of 3,3,5-Triphenyl-2(3H)-furanone (5a)<sup>30</sup>.

A solution of 5a (300 mg, 1 mmol) in benzene (250 mL) was irradiated for 9 h (RPR, 2537 Å). Removal of the solvent and recrystallization of the residue from methanol gave 240 mg (87%) of 6a<sup>29a,b</sup>, mp 91-92 °C (mixture melting point). Irradiation of 5a (200 mg, 0.64 mmol) in methanol (200 mL) for 9 h and workup as in the earlier case gave 120 mg (60%) of 6a, mp 91-92 °C (mixture melting point).

In a repeat run, a solution of 5a (200 mg, 0.64 mmol) in acetone (150 mL) was photolysed for 6 h, under analogous conditions. The residual solid, on removal of the solvent,

was chromatographed over silica gel. Elution with petroleum ether gave 128 mg (65%) of the phenanthro[9,10-c]furanone 9a,<sup>15</sup> mp 259–260 °C (mixture melting point), after recrystallization from methanol. Further elution of the column with a mixture (1:4) of benzene and petroleum ether gave 30 mg (15%) of 7a,<sup>15</sup> mp 124–125 °C (mixture melting point), after recrystallization from methanol. In another experiment, a solution of 5a (100 mg, 0.32 mmol) in benzene (200 mL), containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å), using a 2 mM solution of naphthalene in benzene as filter. Workup as in the earlier case gave 50 mg (51%) of 9a, mp 259–260 °C (mixture melting point) and 20 mg (20%) of 7a, mp 124–125 °C (mixture melting point).

In another run, a solution of 5a (300 mg, 1 mmol) in methanol (200 mL) was irradiated for 3 h (RPR, 3500 Å) in the presence of acetophenone (120 mg, 1 mmol). Removal of the solvent under vacuum gave 250 mg (75%) of 23, mp 146–147 °C (lit.<sup>15</sup> mp 142–143 °C), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 3020, 2990, 2975, 2940 (CH), 1770 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 248 nm ( $\epsilon$ , 9,900), 258 (sh, 8,000), 312 (1,000).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.26 (s, 3 H, methoxy), 4.26 (d, 1 H,  $J = 8.0$  Hz, methine), 5.1 (d, 1 H,  $J = 8.0$  Hz, methine) and 7.08 (m, 15 H, aromatic).

$^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  50.71, 51.49, 59.84, 110.22, 126.78, 126.86, 127.71, 127.89, 127.99, 128.49, 129.14, 129.29, 133.00, 134.72, 135.12 and 175.89 ( $\text{C}=\text{O}$ ).

Transformation of 23 to 7a. A mixture of 23 (60 mg, 0.17 mmol) and stannous chloride (140 mg) in glacial acetic acid (7 mL) was refluxed for 3 h. The mixture, on cooling, was treated with water and extracted with methylene chloride. The methylene chloride-extract was washed with a 5% solution of sodium bicarbonate, dried over sodium sulphate, and removed the solvent under vacuum to give 50 mg (91%) of 7a, mp 124–125  $^\circ\text{C}$  (mixture melting point), after recrystallization from methanol.

I.4.4 Photolysis of 3,5-Diphenyl-3-(4-methylphenyl)-2(3H)-furanone (5b). Irradiation of a solution of 5b (490 mg, 1.5 mmol) in benzene (200 mL) for 3 h (RPR, 3000 Å) and removal of the solvent under vacuum gave a solid, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 60 mg (12%) of the unchanged starting material (5b), mp 109–110  $^\circ\text{C}$  (mixture melting point), after recrystallization from ethanol. Further

elution with a mixture (1:1) of benzene and petroleum ether gave 377 mg (84%) of 6b, mp 105-106 °C, after recrystallization from petroleum ether.

IR spectrum  $\nu_{\max}$  (KBr): 3075, 3050, 3020, 2930 (CH), 1660 (C=O) and 1585 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 240 nm ( $\epsilon$ , 16,200), 335 (12,400).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.35 (s, 3 H, methyl) and 7.48 (m, 15 H, aromatic and vinylic).

Mass spectrum,  $m/e$  (relative intensity): 298 ( $\text{M}^+$ , 100), 283 ( $\text{M}^+ - \text{CH}_3$ , 53), 221 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 24), 105 ( $\text{C}_6\text{H}_5\text{CO}^+$ , 20) and other peaks.

Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ : C, 88.59; H, 6.04. Found: C, 88.62; H, 5.98.

In a repeat run, 5b (600 mg, 1.8 mmol) in methanol (400 mL) was photolysed for 4 h (RPR, 3000 Å) and worked up as in the earlier case to give 82 mg (14%) of the unchanged starting material (5b), mp 109-110 °C (mixture melting point) and 332 mg (60%) of 6b, mp 105-106 °C (mixture melting point).

In another experiment, a solution of 5b (326 mg, 1 mmol) in benzene (150 mL) containing acetophenone (60 mg, 0.5 mmol)

was irradiated for 3 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 150 mg (46%) of a mixture of the phenanthrofurones 9b and 11b in a 3:2 ratio (by  $^1\text{H}$  NMR). Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 98 mg (30%) of a mixture of the furanones 7b and 10b in a 3:2 ratio (by  $^1\text{H}$  NMR).

The mixture of phenanthrofurones 9b and 11b was separated by fractional crystallization from methanol-benzene mixture. The less soluble isomer was identified as 6-methyl-3-phenylphenanthro[9,10-c]furan-1(3H)-one (11b), mp 256-258 °C.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3050, 3020, 2900 (CH), 1750 (C=O), 1630 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 235 nm ( $\epsilon$ , 41,100), 252 (40,700), 261 (41,400), 282 (11,300), 312 (9,300).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.30 (s, 3 H, methyl), 6.18 (s, 1 H, methine), 7.24 (m, 10 H, aromatic), 8.43 and 9.56 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Mass spectrum,  $m/e$  (relative intensity): 324 ( $\text{M}^+$ , 24), 323 ( $\text{M}^+ - \text{H}$ , 18), 293 ( $\text{M}^+ - \text{H}$ , - CO, 6), 218 ( $\text{M}^+ - \text{H}$ , -  $\text{COC}_6\text{H}_5$ , 100) and other peaks.

Anal. Calcd for  $C_{23}H_{16}O_2$ : C, 85.19; H, 4.94. Found: C, 85.52; H, 4.77.

The more soluble isomer 9b was isolated from the mother liquor through repeated column chromatography over silica gel and recrystallization from methanol, mp 264–265 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 3020, 2960, 2900 (CH), 1750 (C=O) and 1620 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 236 nm ( $\epsilon$ , 34,300), 253 (38,200), 262 (41,700).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.33 (s, 3 H, methyl), 6.16 (s, 1 H, methine), 7.28 (m, 10 H, aromatic), 8.26 and 9.33 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Mass spectrum,  $m/e$  (relative intensity): 324 ( $\text{M}^+$ , 25), 323 ( $\text{M}^+ - \text{H}$ , 21), 293 ( $\text{M}^+ - \text{H} - \text{CO}$ , 5), 218 ( $\text{M}^+ - \text{H} - \text{C}_6\text{H}_5\text{CO}$ , 100) and other peaks.

Anal. Calcd for  $C_{23}H_{16}O_2$ : C, 85.19; H, 4.94. Found: C, 85.47; H, 4.98.

Independent Synthesis of 10b. A mixture of  $\alpha$ -bromodesoxybenzoin<sup>15</sup> (17a, 2.76 g, 10 mmol), potassium *p*-methylphenylacetate (18b, 1.89 g, 10 mmol) and 18-crown-6 (300 mg) in acetonitrile (50 mL) was refluxed for 1 h. The precipitated salt was filtered off and the solvent was removed under vacuum

to give an oil, which was passed through a small silica gel column and recrystallized from methanol to give 2.0 g (58%) of benzoin p-methylphenylacetate (19b), mp 101-102 °C.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3060, 3020, 2940, 2920 (CH), 1735, 1680 (C=O) and 1590 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.32 (s, 3 H, methyl), 3.76 (s, 2 H, methylene), 6.86 (s, 1 H, methine) and 7.6 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_3$ : C, 80.23; H, 5.81. Found: C, 80.57; H, 6.02.

To a stirred solution of 19b (340 mg, 1 mmol) in dry dimethyl sulfoxide (25 mL), sodium hydride (24 mg, 1 mmol) was gradually added and the stirring was continued for 2 h at room temperature and then at 60-70 °C for another 10 minutes. The mixture was cooled, poured into cold water and extracted with ether. The ether-extract, after washing with dilute hydrochloric acid (2 N, 50 mL) and water, was dried over anhydrous sodium sulphate. Removal of the solvent gave 200 mg (61%) of 4,5-diphenyl-3-(4-methylphenyl)-2(5H)-furanone (10b), mp 127-128 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3060, 3030, 2910 (CH), 1747 (C=O), 1630 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 224 nm ( $\epsilon$ , 24,600), 266 (11,700), 283 (12,700).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.33 (s, 3 H, methyl), 6.23 (s, 1 H, methine) and 7.39 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 84.94; H, 5.37.

Preparation of the Phenanthrofuranone 11b. A solution of 10b (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 37 mg (75%) of 11b, mp 256–258 °C (mixture melting point).

Preparation of the Phenanthrofuranone 9b. A solution of 7b<sup>15</sup> (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 40 mg (81%) of 9b, mp 264–265 °C (mixture melting point).

I.4.5 Photolysis of 3,5-Diphenyl-3-(4-methoxyphenyl)-2(3H)-furanone (5c). A solution of 5c (510 mg, 1.5 mmol) in benzene (200 mL) was irradiated for 4 h (RPR, 3000 Å). The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 157 mg (31%) of the unchanged



starting material (5c), mp 92-93 °C (mixture melting point), after recrystallization from ethanol. Further elution with a mixture (1:1) of benzene and petroleum ether gave 300 mg (64%) of 6c, mp 74-75 °C, after recrystallization from petroleum ether.

IR spectrum  $\nu_{\max}$  (KBr): 3020, 2930, 2830 (CH), 1645 (C=O) and 1580 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 238 nm ( $\epsilon$ , 17,800), 336 (13,300).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.80 (s, 3 H, methoxy) and 7.5 (m, 15 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}_2$ : C, 84.08; H, 5.73. Found: C, 83.82; H, 5.61.

Irradiation of 5c (510 mg, 1.5 mmol) in methanol (200 mL), under analogous conditions gave 152 mg (30%) of the unchanged starting material (5c), mp 92-93 °C (mixture melting point), after recrystallization from ethanol, and 300 mg (64%) of 6c, mp 74-75 °C (mixture melting point), after recrystallization from petroleum ether.

In a repeat experiment, a solution of 5c (100 mg, 0.29 mmol) in benzene (150 mL) containing acetophenone (30 mg,

0.25 mmol) was irradiated for 3 h (RPR, 3500 Å) using a 2 mM naphthalene solution in benzene as filter. On removal of the solvent, the residue was chromatographed over silica gel. Elution with a mixture (1:1) of benzene and petroleum ether gave 49 mg (49%) of a mixture of phenanthrofurones 9c and 11c in a 2:3 ratio (by  $^1\text{H}$  NMR). Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 29 mg (29%) of a mixture of 2(5H)-furones 7c and 10c in a 2:3 ratio (by  $^1\text{H}$  NMR).

Independent Synthesis of 10c. A solution of  $\alpha$ -bromo-desoxybenzoin (17a, 2.76 g, 10 mmol), potassium p-methoxyphenylacetate (18c, 2.05 g, 10 mmol) and 18-crown-6 (250 mg) in acetonitrile (50 mL) was refluxed for 1 h. Removal of the precipitated salt and the solvent and workup as in the earlier case gave benzoin p-methoxyphenylacetate (19d), mp 108-109 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3080, 3020, 3000, 2960, 2900 (CH), 1740, 1690 (C=O) and 1590 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.76 (s, 2 H, methylene), 3.82 (s, 3 H, methoxy), 6.75 (s, 1 H, methine) and 7.5 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_4$ : C, 76.67; H, 5.56. Found: C, 77.01; H, 5.80.

To a solution of 19d (720 mg, 2 mmol) in dry dimethyl sulfoxide (50 mL), sodium hydride (48 mg, 2 mmol) was added while stirring. The stirring was continued at room temperature for 2 h and then at 60–70 °C for 10 minutes. Workup of the mixture as in the case of 10b gave 250 mg (35%) of 10c, mp 126–127 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 3035, 3000, 2960 (CH), 1750 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 228 nm ( $\epsilon$ , 22,000), 270 (10,200), 300 (9,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.81 (s, 3 H, methoxy), 6.20 (s, 1 H, methine) and 7.13 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_3$ : C, 80.70; H, 5.26. Found: C, 80.27; H, 5.68.

Preparation of the Phenanthrofuranone 11c. A solution of 10c (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 42 mg (85%) of 11c, mp 216–218 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3070, 3030, 2900 (CH), 1750 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 242 nm ( $\epsilon$ , 40,400), 248 (39,900), 262 (sh, 29,300), 290 (8,000), 322 (6,900).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.60 (s, 3 H, methoxy), 6.20 (s, 1 H, methine), 7.41 (m, 10 H, aromatic), 8.43 and 9.33 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Anal. Calcd for  $\text{C}_{23}\text{H}_{16}\text{O}_3$ : C, 81.18; H, 4.71. Found: C, 81.25; H, 4.52.

Preparation of the Phenanthrofuraneone 9c. A solution of  $7\text{c}^{15}$  (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and the solvent was removed under vacuum to give 40 mg (81%) of 9c, mp 223–225 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3060, 3020, 3000, 2970, 2940 (CH), 1740 (C=O), 1610 and 1590 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 243 nm ( $\epsilon$ , 27,300), 260 (29,000), 278 (12,300), 322 (10,200).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  4.0 (s, 3 H, methoxy), 6.60 (s, 1 H, methine), 7.55 (m, 10 H, aromatic), 8.66 and 9.23 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Anal. Calcd for  $\text{C}_{23}\text{H}_{16}\text{O}_3$ : C, 81.18; H, 4.71. Found: C, 81.42; H, 4.93.

I.4.6 Photolysis of 3-(4-Cyanophenyl)-3,5-diphenyl-2(3H)-furanone (5d). A solution of 5d (337 mg, 1 mmol) in benzene (200 mL) was irradiated for 3 h (RPR, 3000 Å). The solvent

was removed under vacuum and the residue was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 34 mg (10%) of the unchanged starting material 5d, mp 114-115 °C (mixture melting point), after recrystallization from a mixture (1:1) of carbon tetrachloride and petroleum ether. Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 260 mg (85%) of 6d, mp 113-114 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3050, 3020 (CH), 2220 (C $\equiv$ N), 1650 (C=O) and 1585 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 250 nm ( $\epsilon$ , 22,700), 268 (16,700), 296 (15,400).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  7.6 (m, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{NO}$ : C, 85.44; H, 4.85; N, 4.53.  
Found: C, 85.01; H, 4.92; N, 4.67.

Irradiation of 5d (337 mg, 1 mmol in methanol (200 mL) under analogous conditions gave 30 mg (9%) of the unchanged starting material (5d), mp 114-115 °C (mixture melting point), after recrystallization from a mixture (1:1) of carbon tetrachloride and petroleum ether and 270 mg (87%) of 6d, mp 113-114 °C (mixture melting point), after recrystallization from methanol.

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In a repeat experiment, a solution of 5d (300 mg, 0.9 mmol) in benzene (300 mL) containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å) using a 2 mM naphthalene solution in benzene as filter. Removal of the solvent gave a residue, which was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 120 mg (40%) of the dimer 12d, mp > 360 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 3025 (CH), 2220 (C≡N) and 1760 (C=O)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (acetonitrile): 234 nm ( $\epsilon$ , 40,600), 270 (5,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  5.07 (s, 2 H, methine) and 7.21 (m, 28 H, aromatic).

Mass spectrum,  $m/e$  (relative intensity): 674 ( $\text{M}^+$ , 2), 337 ( $\text{M}^+/2$ , 11), 336 ( $\text{M}^+/2 - \text{H}$ , 43), 231 ( $\text{M}^+/2 - \text{H}$ , -  $\text{COC}_6\text{H}_5$ , 100) and other peaks.

Anal. Calcd for  $\text{C}_{46}\text{H}_{30}\text{N}_2\text{O}_4$ : C, 81.90; H, 4.45; N, 4.15. Found: C, 81.87; H, 4.35; N, 3.85.

Further elution of the column with a mixture (3:2) of benzene and petroleum ether gave 55 mg (18%) of the

phenanthrofuranone 9d, mp 265-267 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3080, 3050, 3010 (CH), 2220 (C $\equiv$ N), 1740 (C=O) and 1595 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 233 nm ( $\epsilon$ , 37,600), 250 (38,700), 260 (sh, 35,600), 284 (sh, 10,100), 320 (10,200).

$^1\text{H}$  NMR spectrum (DMSO- $d_6$ ):  $\delta$  7.0 (m, 11 H, aromatic and methine), 8.3 and 8.8 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Anal. Calcd for  $\text{C}_{23}\text{H}_{13}\text{NO}_2$ : C, 82.39; H, 3.88; N, 4.18. Found: C, 81.91; H, 3.52; N, 4.15.

Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 48 mg (16%) of 7d, mp 177-178 °C (mixture melting point) (lit.<sup>15</sup> mp 178-179 °C), after recrystallization from methanol.

Preparation of the Phenanthrofuranone 9d. A solution of 7d (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å). Removal of the solvent under vacuum and recrystallization of the residue from methanol gave 35 mg (71%) of 9d, mp 265-267 °C (mixture melting point).

I.4.7 Photolysis of 3-(4-Chlorophenyl)-3,5-diphenyl-2(3H)-furanone (5e). A solution of 5e (200 mg, 0.58 mmol) in benzene (200 mL) was irradiated for 4 h (RPR, 3000 Å).

Removal of the solvent under vacuum and recrystallization of the residue from petroleum ether gave 160 mg (82%) of 6e, mp 106-107 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3040, 3010 (CH), 1645 (C=O) and 1580 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 232 nm ( $\epsilon$ , 16,800), 312 (10,900).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  7.55 (m, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{21}\text{H}_{15}\text{ClO}$ : C, 79.25; H, 4.72. Found: C, 79.53; H, 4.86.

In another experiment, 100 mg (0.29 mmol) of 5e in methanol (150 mL) was irradiated under analogous conditions and worked up to give 75 mg (76%) of 6e, mp 106-107 °C (mixture melting point), after recrystallization from petroleum ether.

In a repeat experiment, a solution of 5e (150 mg, 0.44 mmol) in benzene (450 mL) containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å). The residue, after removal of the solvent under vacuum, was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 80 mg (53%) of the dimer 12e, mp > 360 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol.



IR spectrum  $\nu_{\max}$  (KBr): 3050, 3020 (CH), 1760 (C=O) and 1595 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (acetonitrile): 232 nm ( $\epsilon$ , 23,000), 260 (6,100).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  5.0 (s, 2 H, methine) and 7.16 (m, 28 H, aromatic).

Anal. Calcd for  $\text{C}_{44}\text{H}_{30}\text{Cl}_2\text{O}_4$ : C, 76.30; H, 4.33. Found: C, 76.33; H, 3.94.

Further elution of the column with a mixture (3:2) of benzene and petroleum ether gave 20 mg (13%) of the phenanthrofurane 9e, mp 272-274  $^\circ\text{C}$ , after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 3020 (CH), 1740 (C=O) and 1590 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 234 nm ( $\epsilon$ , 27,900), 248 (sh, 25,900), 260 (29,300), 278 (sh, 9,800), 310 (8,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  6.70 (s, 1 H, methine), 7.66 (m, 10 H, aromatic), 8.75 and 9.33 (m, 2 H,  $\text{H}^7$  and  $\text{H}^8$ ).

Anal. Calcd for  $\text{C}_{22}\text{H}_{13}\text{ClO}_2$ : C, 76.74; H, 3.76. Found: C, 76.43; H, 3.54.

Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 20 mg (13%) of the 2(5H)-

furanone 7e, mp 173-174 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3050, 3020 (CH), 1750 (C=O) and 1590 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 220 nm ( $\epsilon$ , 25,400), 260 (11,200), 290 (1,000).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  6.26 (s, 1 H, methine) and 7.55 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{ClO}_2$ : C, 76.30; H, 4.34. Found: C, 76.66; H, 4.08.

Independent Synthesis of 7e. To an ether solution of 4-chlorodesoxybenzoin (2.3 g, 10 mmol in 25 mL) was added a solution of bromine (1.6 g, 10 mmol) in ether (10 mL) with stirring for 0.5 h, after which time the reaction mixture was quenched by the addition of a 1% aqueous solution of sodium thiosulphate. The organic layer was washed with water, dried over anhydrous magnesium sulphate and the solvent was removed under vacuum to give a nearly quantitative yield of 4-chlorodesyl bromide (17e). The crude bromoketone 17e was taken up in acetonitrile (50 mL) and refluxed for 2 h with potassium phenylacetate (18a, 1.75 g, 10 mmol) and 18-crown-6 (300 mg). Workup of the reaction mixture as in the earlier cases gave 2.0 g (55%)

of 4-chlorobenzoin phenylacetate (19f), mp 64-65 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3090, 3060, 3030, 2920 (CH), 1735, 1695 (C=O) and 1590 (C=C)  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.83 (s, 2 H, methylene), 6.80 (s, 1 H, methine) and 7.55 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{22}\text{H}_{17}\text{ClO}_3$ : C, 72.53; H, 4.67. Found: C, 72.26; H, 4.41.

To a solution of 19f (728 mg, 2 mmol) in dry dimethyl sulfoxide (50 mL), sodium hydride (48 mg, 2 mmol) was added and the mixture was stirred at 20 °C for 2 h and later at 60-70 °C for 10 minutes. Workup as in the earlier cases gave 350 mg (50%) of 7e, mp 173-174 °C (mixture melting point), after recrystallization from methanol.

Preparation of the Phenanthrofuranone 9e. A solution of 7e (50 mg, 0.14 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and the solvent was removed under vacuum to yield a residue, which was crystallized from methanol to give 35 mg (71%) of 9e, mp 272-274 °C (mixture melting point).

I.4.8 Laser Flash Photolysis.<sup>33</sup> For laser flash photolysis use was made of a computer controlled set-up described

elsewhere.<sup>41</sup> The pulsed laser sources were: Lambda-Physik EMG 101 excimer (248 and 308 nm,  $\sim 20$  ns), Molelectron UV-400 nitrogen (337.1 nm,  $\sim 8$  ns) and Quanta-Ray DCR-1 Nd-YAG (third harmonic, 355 nm,  $\sim 6$  ns). The laser intensities were attenuated and kept in the range 2-10 mJ/pulse. For transient spectra, a flow cell was used. Deoxygenation of solutions was effected by saturation with argon.

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## CHAPTER II

### PHOTOCHEMICAL AND THERMAL TRANSFORMATIONS OF A FEW 3-BENZYL-2(3H)-FURANONES AND RELATED SUBSTRATES

#### II.1 ABSTRACT

Photochemical and thermal transformations of a few 2(3H)-furanones such as 3-benzyl-3,5-diphenyl-2(3H)-furanone (2a), 3-benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b), 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone (2c), 3,3-dibenzyl-5-phenyl-2(3H)-furanone (2d), 3-benzyl-3-phenylphenanthro[9,10-b]furan-2(3H)-one (9) and 3-benzoyl-3,5-diphenyl-2(3H)-furanone (15) have been examined. In order to understand the mechanistic details of these reactions, the electron-transfer sensitization reactions of some of these furanones and also of some bis(benzofuranones) such as 5,5'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18b) and 6,6'-dimethyl-3,3'-diphenyl-3,3'-bibenzo [b] furan-2,2'(3H,3'H)-dione (18c) have been studied under steady-state as well as laser flash photolytic conditions.

Irradiation of 2a, for example, in benzene or methanol gave 2,3,5-triphenylfuran (7a) and 1,3,4-triphenyl-



but-3-en-1-one (8a), along with some unchanged starting material. Similar results were obtained when the irradiation of 2b and 2c were carried out under analogous conditions. Irradiation of 2d, under these conditions, gave 8d as the only isolable product. In contrast, the irradiation of 9 gave the phenanthrofurane 10, whereas, 15 under analogous conditions, gave the bisfuranone 14a.

The irradiation of 2a-c under acetophenone sensitization in benzene solution, on the other hand, gave the isomeric furanones 13a-c and the bisfuranones 14a-c, along with some unchanged starting material in each case. Irradiation of 2d, however, gave 13d as the only product. Thermolysis of 2a-d, on the other hand, gave 13a-d in good yields. Upon photoinduced electron-transfer reaction using DCN, 1a,b gave the bisfuranones 14a,b, whereas the bis(benzofuranones) 18b,c, under analogous conditions, gave the benzofuranones 22b,c and the hydroxy lactones 24b,c, along with some unchanged starting material.

Reasonable mechanisms for the formation of the various products in these reactions have been suggested. Laser flash photolysis studies of the electron-transfer reactions indicate that the radical cations from these

substrates fragment, on a nanosecond time scale, to produce furanoxo radicals. These furanoxo radicals have also been proposed as intermediates in acetophenone-sensitized reactions of 2a-d.

## II.2 INTRODUCTION

Photochemical transformations of several 3,3,5-triaryl-2(3H)-furanones based on steady-state irradiation, product analysis, and laser flash photolysis have been presented in the first chapter of this thesis. The two major pathways for the photoreactions of these furanones include a singlet mediated decarbonylation reaction to give the corresponding  $\alpha,\beta$ -unsaturated carbonyl compounds and a triplet mediated aryl group migration to give 3,4,5-triaryl-2(5H)-furanones. The 3,4,5-triaryl-2(5H)-furanones, in turn, undergo further reaction, under the reaction conditions, to give phenanthro-furanones or dimeric products. Based on product analysis and laser flash photolysis studies, we have examined the excited state migratory aptitudes and rates of migration of various aryl groups in these photorearrangements.<sup>1,2</sup>

As part of our continuing interest in the photo-transformations of unsaturated lactones, we have investigated in the present studies, the photochemical and thermal

transformations of several 3-benzyl-3,5-diaryl-2(3H)-furanones and related substrates. The results of these studies are presented in this chapter. It has been observed earlier that the thermal transformations of 2(3H)-furanones are similar to their phototransformations, under direct irradiation conditions and generally give rise to decarbonylation products.<sup>1,3,4</sup> In some cases, however, thermal transformations lead to rearranged products, arising through a [1,3]-sigmatropic shift of the substituent groups.<sup>5,6</sup> The thermal transformations of the related bis(benzofuranones), on the other hand, are known to give rise to a variety of products, arising through radical intermediates.<sup>7,8</sup>

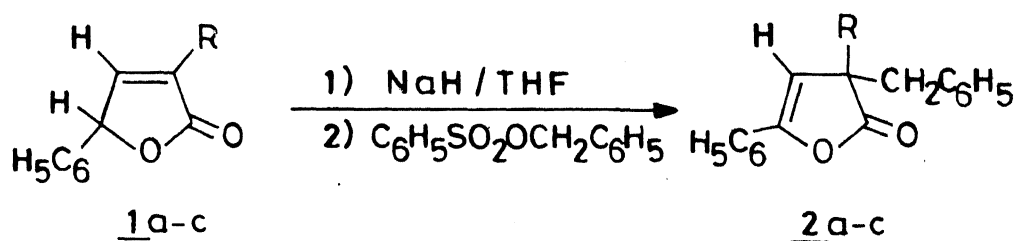
The objective of the present study has been to examine the phototransformations of some selected 2(3H)-furanones and bis(benzofuranones), both under direct, as well as sensitized irradiation conditions and also to generalize the mechanistic pathways of these reactions. To characterize the intermediates involved in these reactions, we have also carried out the steady-state and laser flash photolysis studies of the photo-induced electron-transfer reactions of some representative furanones and bis(benzofuranones). Laser flash photolysis studies have been mainly confined to the photoinduced electron-transfer reactions. These studies provide a

convenient method for the generation and characterization of the same transient species as produced under benzophenone or acetophenone triplet sensitization reactions of these furanones<sup>9</sup> (vide infra). The 2(3H)-furanones and bis(benzofuranones) that were used for these studies include, 3-benzyl-3,5-diphenyl-2(3H)-furanone (2a), 3-benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b), 3-benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone (2c), 3,3-dibenzyl-5-phenyl-2(3H)-furanone (2d), 3-benzyl-3-phenylphenanthro[9,10-b]furan-2(3H)-one (9), 3-benzoyl-3,5-diphenyl-2(3H)-furanone (15), 3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18a), 5,5'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18b), 6,6'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18c) and 7,7'-dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18d).

## II.3 RESULTS AND DISCUSSION

II.3.1 Starting Materials. The furanones 9<sup>1</sup> and 15<sup>10</sup> and the bis(benzofuranones) 18a-d<sup>8</sup> were prepared by reported procedures. The 3-benzyl-2(3H)-furanones 2a-d have been prepared by the route outlined in Scheme II.1. The structures of these furanones 2a-d have been established on the

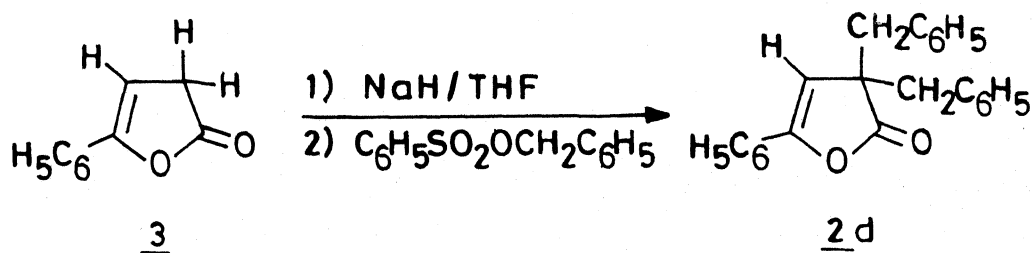
# Scheme II.1



a, R = C<sub>6</sub>H<sub>5</sub>

b, R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

c, R = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>



basis of analytical data and spectral evidence. For example, the IR spectra of all these furanones showed a strong carbonyl absorption band around  $1780\text{ cm}^{-1}$  and a C=C stretching absorption band at  $1650\text{ cm}^{-1}$ , both of which are very characteristic of  $\beta,\gamma$ -unsaturated lactones. In addition, the  $^1\text{H}$  NMR spectra of 2a-c showed a singlet around  $\delta$  3.3-3.6 (2 H), assigned to the benzylic protons and a singlet around  $\delta$  6.0-6.3 (1 H), assigned to the vinylic proton at the C-4 position of the furanones. The aromatic protons, in each case, appeared as a multiplet centred around  $\delta$  7.2-7.5. As a representative example, the  $^1\text{H}$  NMR spectrum of 2b is given in Figure II.1. The  $^1\text{H}$  NMR spectrum of 2d (Figure II.2) was, however, slightly different, in that the protons constituting the two benzylic groups appeared as a quartet. This phenomenon is not unexpected, considering the hindrance to free rotation along the C-C bond, due to the presence of two benzyl groups at the same position of the furanone ring.

II.3.2 Preparative Photochemistry and Product Identification. Irradiation of a solution of the 2(3H)-furanone 2a in benzene and methanol gave a mixture of 2,3,5-triphenylfuran<sup>11</sup> (7a, 8-9%) and 1,3,4-triphenylbut-3-en-1-one (8a, 21-26%), along with some unchanged starting material (34-37%) (Scheme II.2). In contrast, when the irradiation

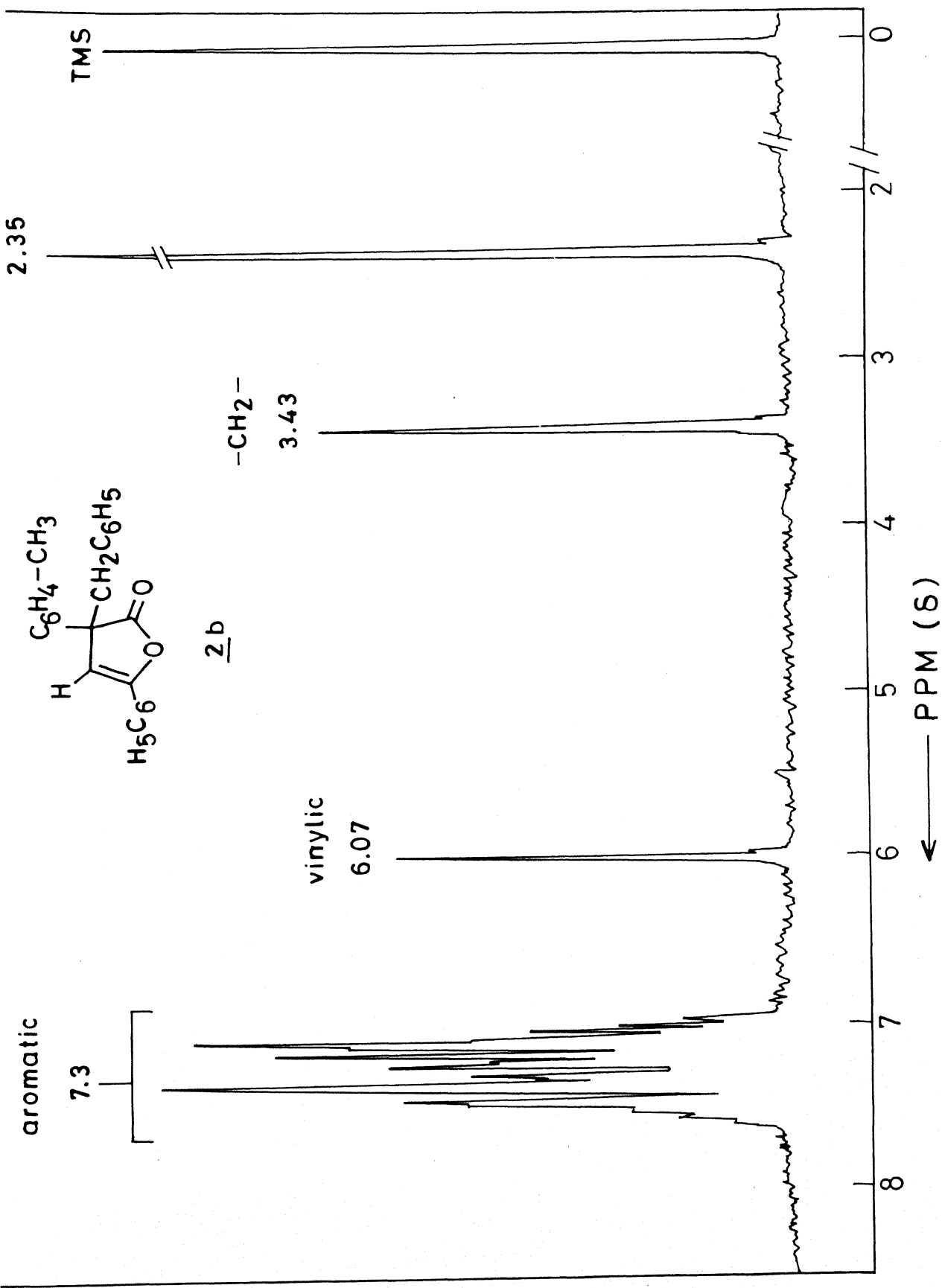


Figure II.1 <sup>1</sup>H NMR spectrum (90 MHz) of 2b.

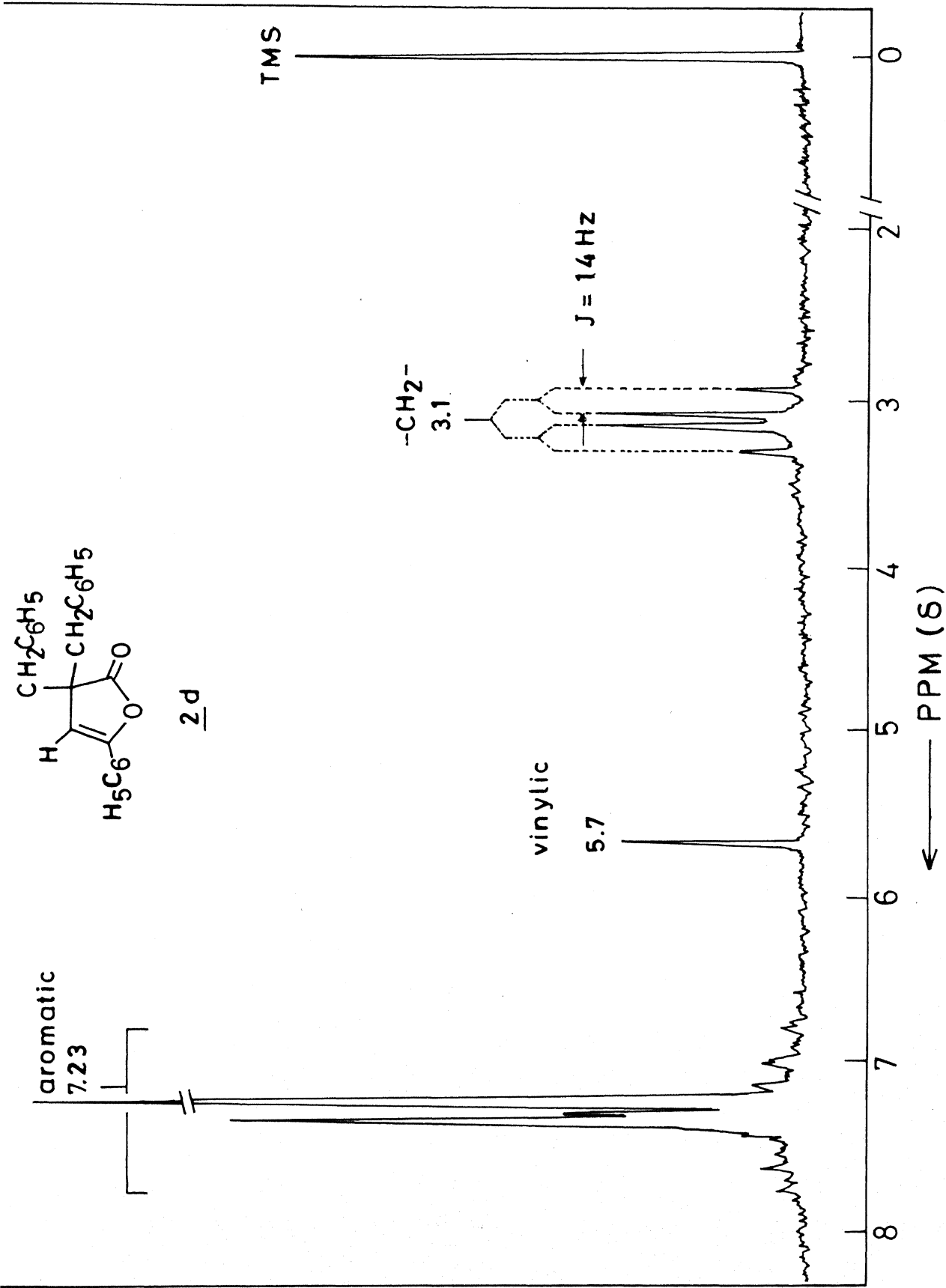


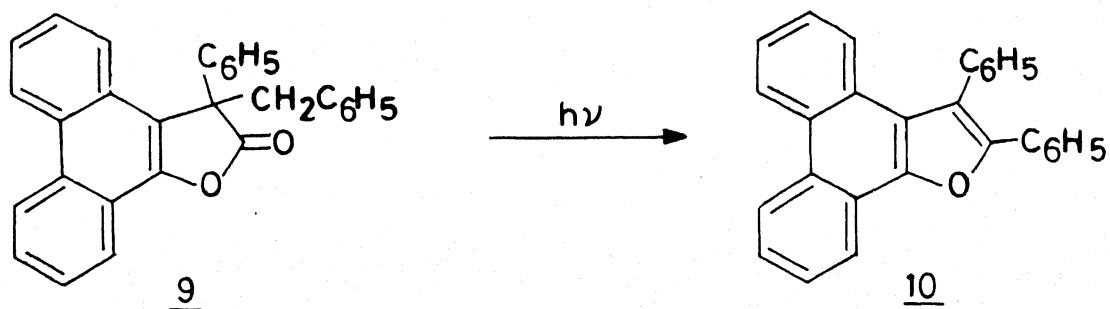
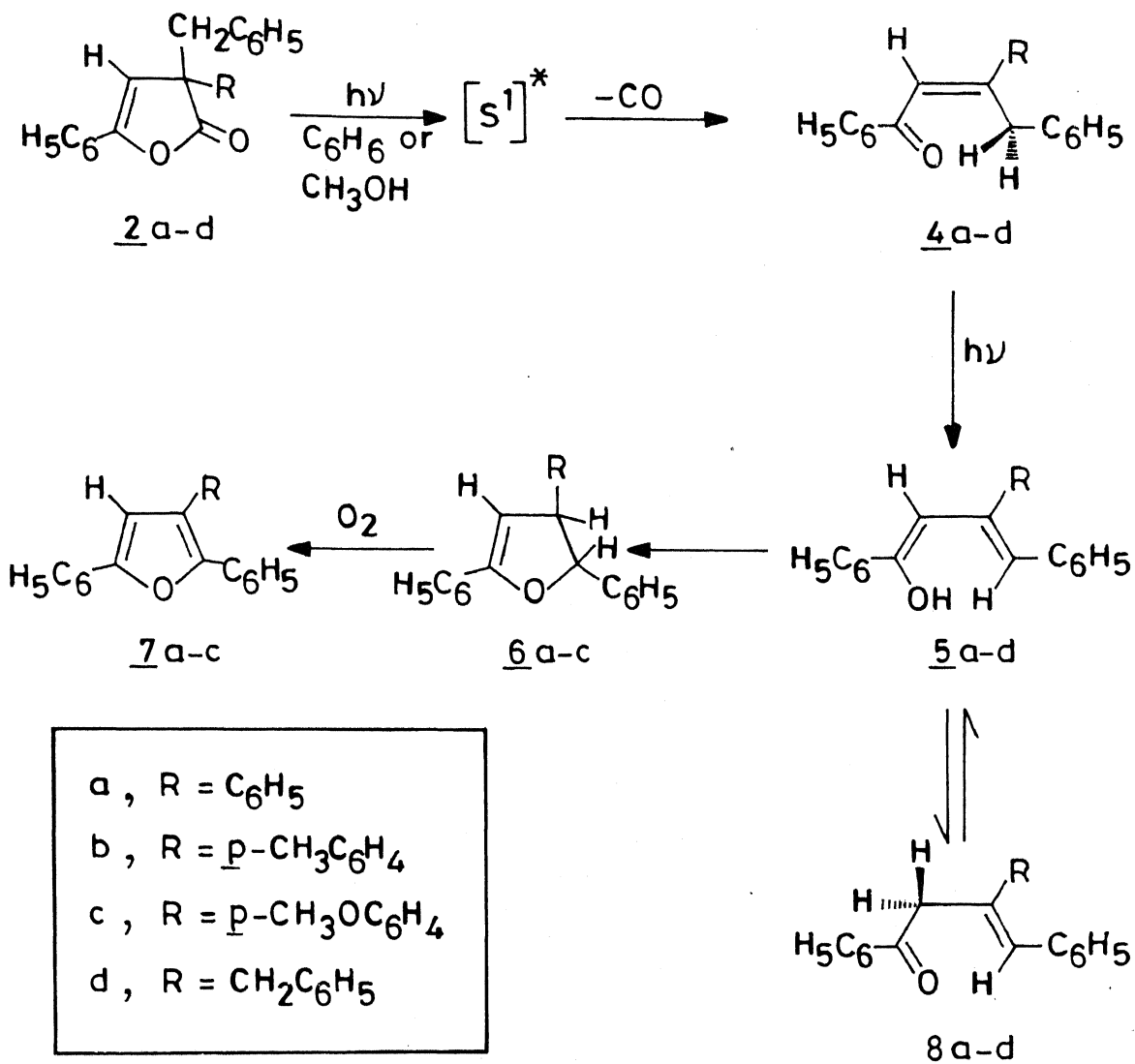
Figure 11.2 <sup>1</sup>H NMR spectrum (90 MHz) of **2d**.



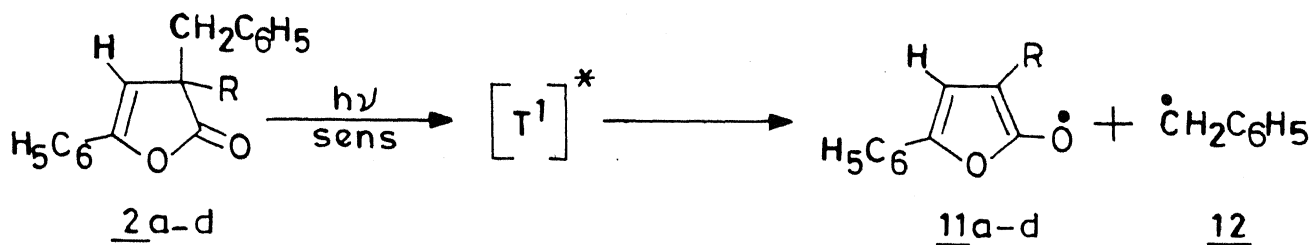
of 2a was carried out in benzene, using acetophenone as sensitizer, under conditions wherein only the sensitizer absorbed all the light, the products obtained were 5-benzyl-3,5-diphenyl-2(5H)-furanone (13a, 35%) and the bisfuranone 14a (27%), besides a 25% recovery of the unchanged starting material (Scheme II.3). On the other hand, when the irradiation of 2a was carried out in acetonitrile under conditions of photoinduced electron-transfer using 1,4-dicyanonaphthalene (DCN), the product obtained was 14a (64%), along with a 25% recovery of the unchanged starting material (Scheme II.4).

In order to shed light on the nature of the excited state species in these photoreactions, we have examined the reactions of different substituted analogues of 2a, under direct, sensitized and electron-transfer irradiation conditions. Thus, the irradiation of 2b in benzene and methanol gave the furan derivative 7b (6-13%) and the butenone derivative 8b (21-31%) in each case, along with some unchanged starting material (40-50%), whereas, irradiation of 2b in benzene using acetophenone as sensitizer gave the rearranged 2(5H)-furanone 13b (50%) and the bisfuranone 14b (7%), along with a 25% recovery of the unchanged starting material. Photoinduced electron-transfer reaction of 2b, on the other hand, gave the bisfuranone 14b in a 66% yield, along with a 12% recovery of the unchanged starting material.

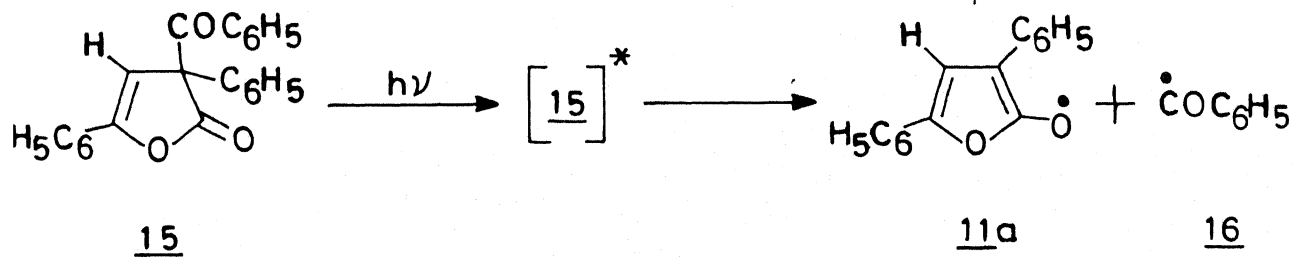
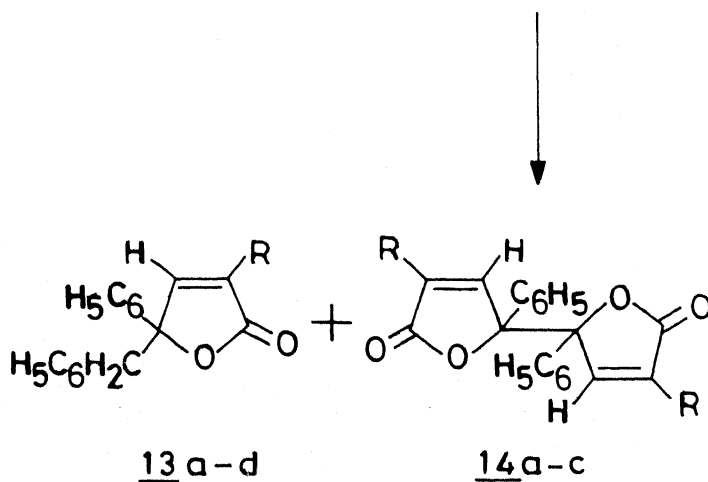
# Scheme II.2



### Scheme II.3



- a , R = C<sub>6</sub>H<sub>5</sub>  
b , R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>  
c , R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>  
d , R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>



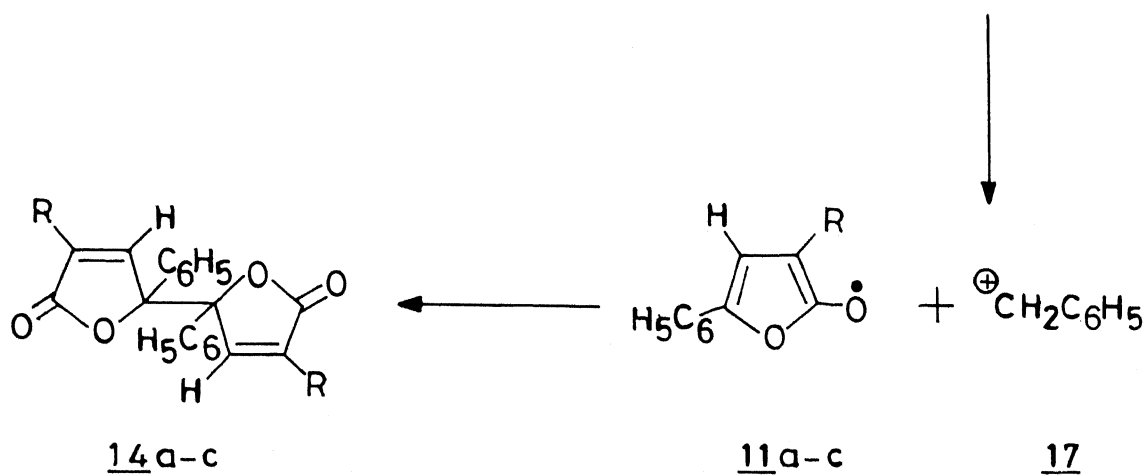
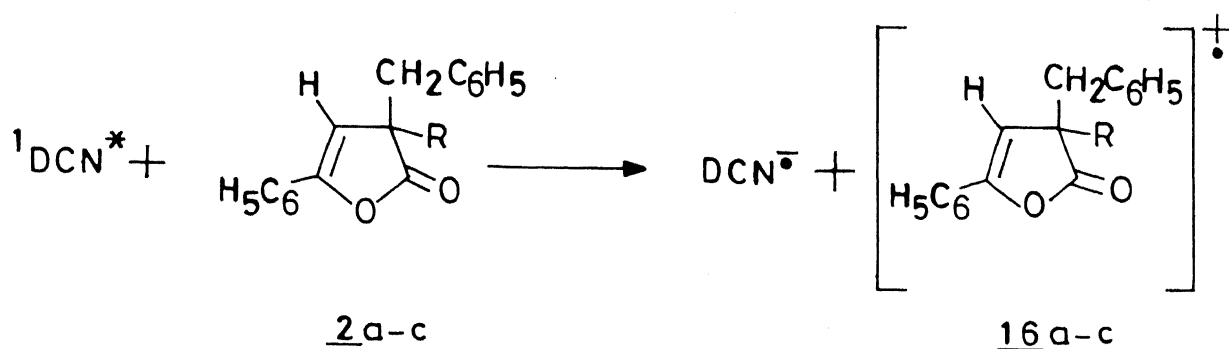
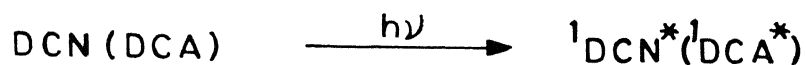
Likewise, the irradiation of 2c in benzene and methanol gave the furan derivative 7c (8-11%) and the butenone derivative 8c (24-25%), along with a 50% recovery of the unchanged starting material, in each case. Irradiation of 2c in benzene using acetophenone as sensitizer gave a mixture of the 2(5H)-furanone 13c (48%) and the bisfuranone 14c (6%), in addition to a 25% recovery of the unchanged starting material.

Irradiation of 2d in benzene and methanol, however, gave only 1,4-diphenyl-3-benzylbut-3-en-1-one (8d) in 80% and 83% yields, respectively. Sensitized irradiation of 2d using acetophenone gave the rearranged lactone 13d (23%), along with a 58% recovery of the unchanged starting material.

Irradiation of the phenanthrofurane 9 in benzene and methanol, on the other hand, gave 10 in 16% and 21% yields, respectively, along with some unchanged starting material (20-45%), in each case. In contrast, irradiation of the benzoyl derivative 15 in benzene and methanol or under acetophenone sensitization gave 14a (70-75%), as the only isolable product.

Direct irradiations of the bis(benzofuranones) 18a-d have been examined earlier in this laboratory.<sup>1</sup> In the present investigation, we have studied the electron-transfer

# Scheme 11.4



a , R = C<sub>6</sub>H<sub>5</sub>

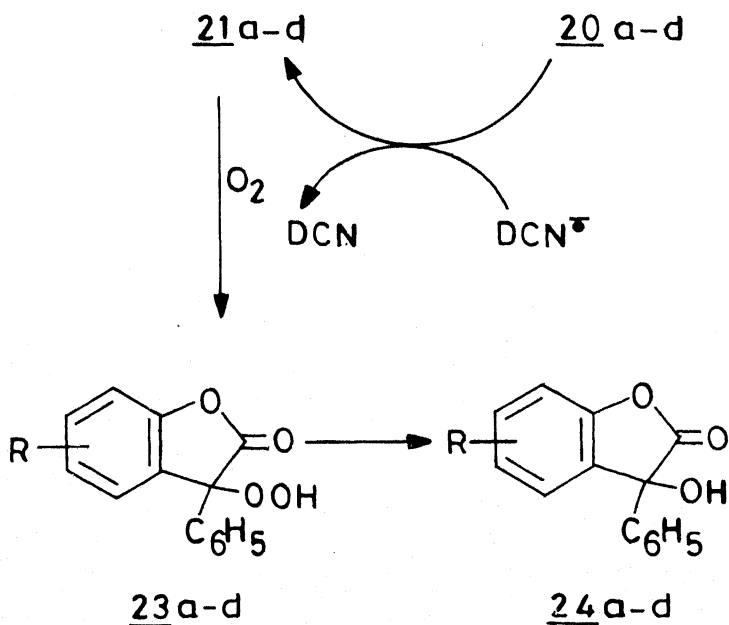
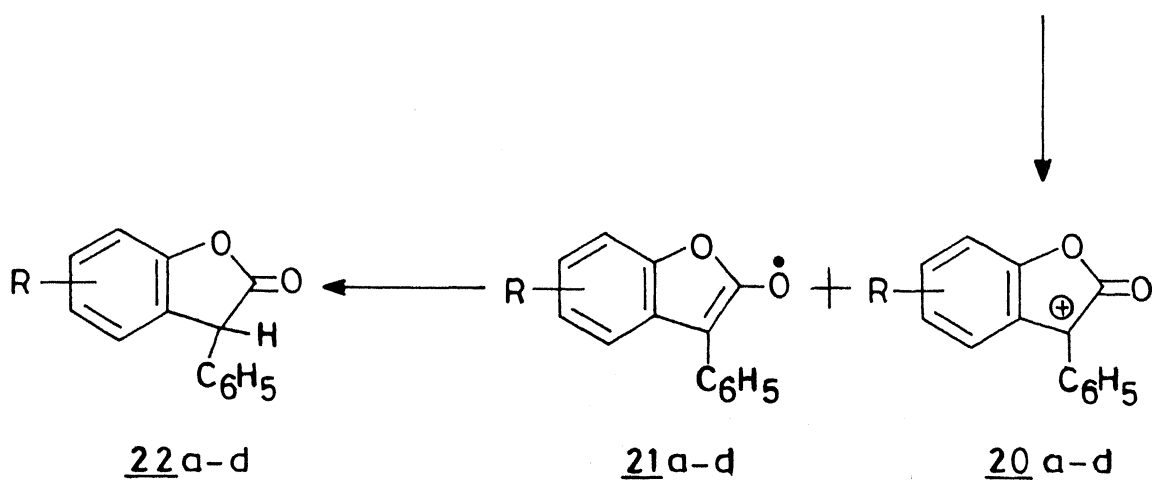
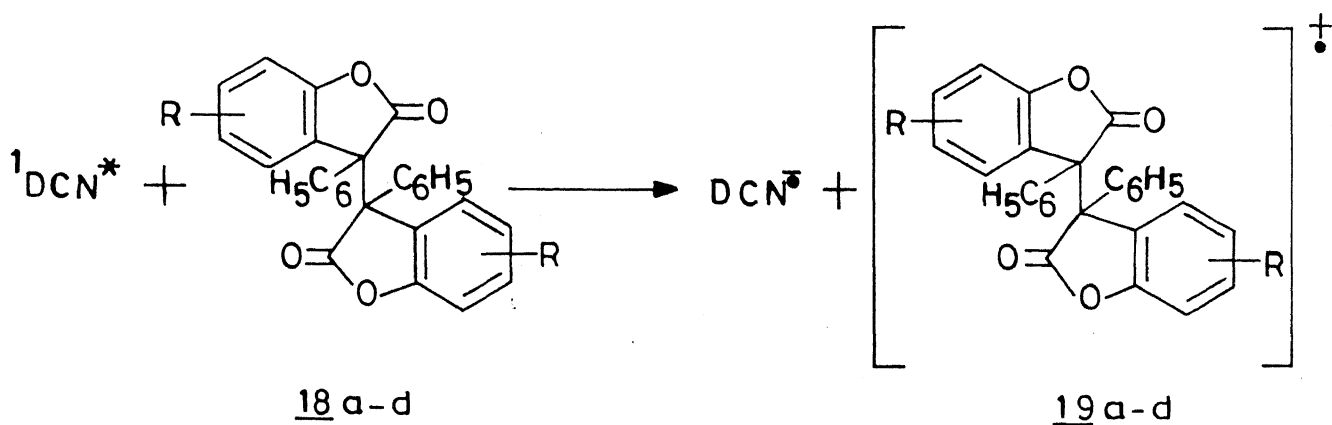
b , R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

c , R = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>

reactions of some of these lactones. Thus, the irradiation of 18b in acetonitrile in the presence of DCN gave the benzofuranone 22b and the hydroxylactone 24b in 33% and 19% yields, respectively, besides the recovery of some unchanged starting material (44%). Similarly, the irradiation of 18c, under analogous conditions, gave a 33% yield of 22c and 23% yield of 24c, along with a 35% recovery of the unchanged starting material (Scheme II.5).

The structures of all the products have been established on the basis of analytical results, spectral evidence and comparison with authentic samples, wherever applicable. For example, the IR spectra of the  $\beta,\gamma$ -unsaturated ketones 8a-d showed a carbonyl absorption band at  $1670\text{--}1685\text{ cm}^{-1}$ . The  $^1\text{H}$  NMR spectra of 8a-c showed a singlet at  $\delta$  4.3–4.5 (2 H), assigned to the methylene protons and a singlet at  $\delta$  6.6–7.1 (1 H), assigned to the vinylic proton. The aromatic protons, in each case, appeared as a multiplet centred around  $\delta$  7.5–7.7. The  $^1\text{H}$  NMR spectrum of a representative example, 8a is shown in Figure II.3. The  $^1\text{H}$  NMR spectrum of 8d (Figure II.4) was, however, slightly different in that the methylene protons appeared at a slightly higher field ( $\delta$  3.97) than in the other cases. The benzylic protons appeared at  $\delta$  3.43 (s, 2 H), the vinylic proton at  $\delta$  6.73 (s, 1 H) and the aromatic protons as a multiplet (15 H) around  $\delta$  7.47.

# Scheme 11.5



- a , R = H

b , R = 5-CH<sub>3</sub>

c , R = 6-CH<sub>3</sub>

d , R = 7-CH<sub>3</sub>

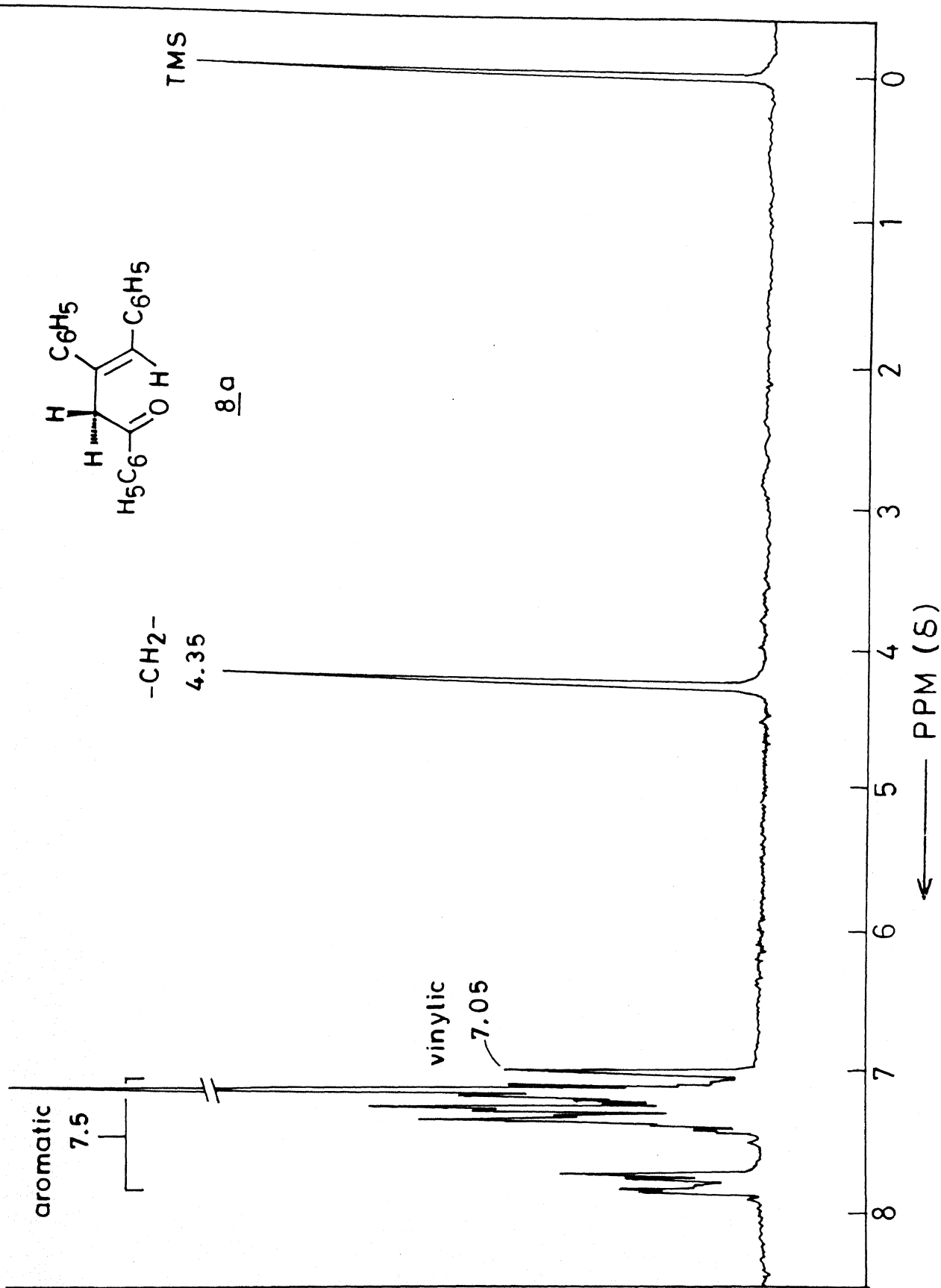
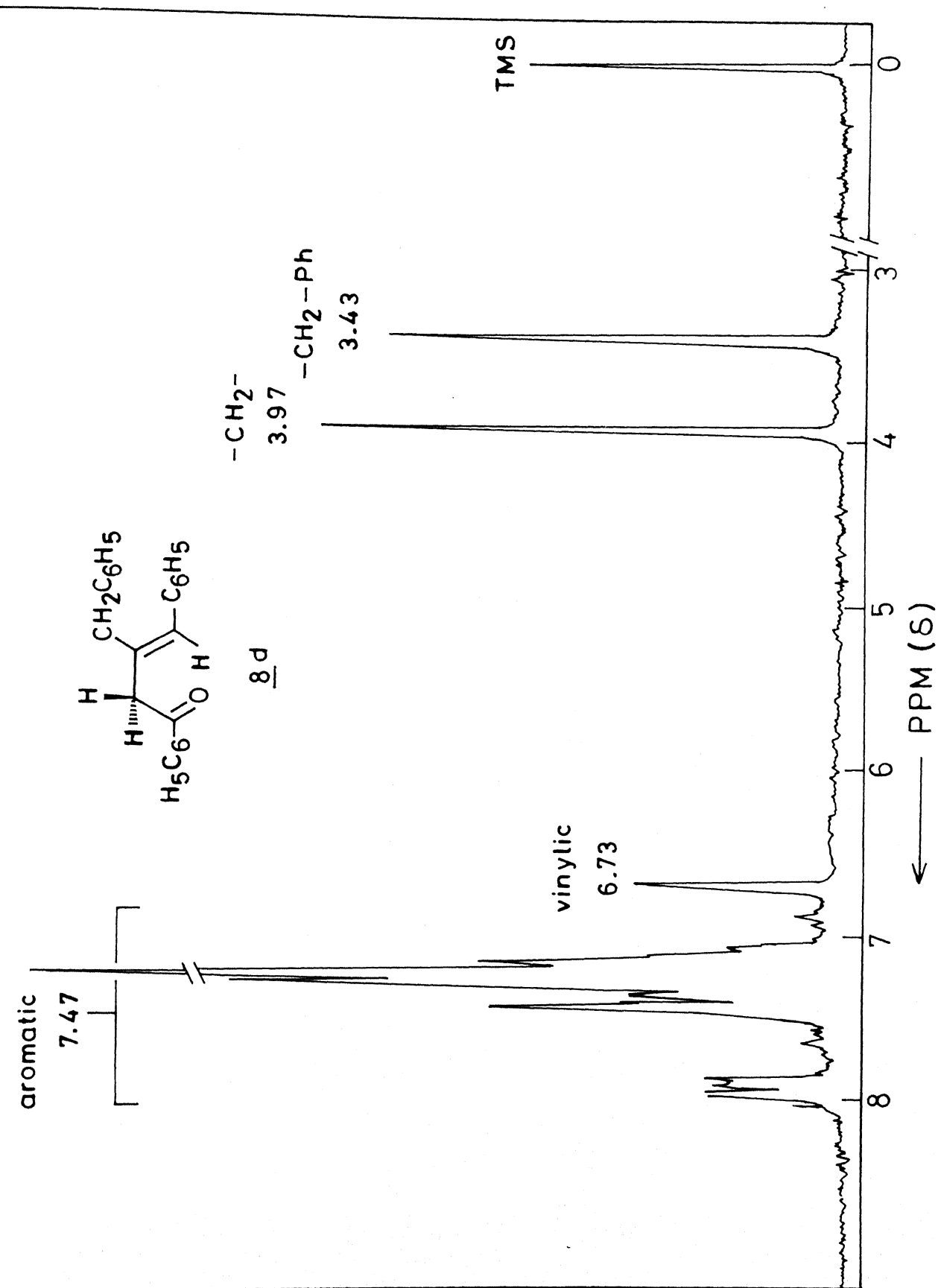


Figure II.3  $^1\text{H}$  NMR spectrum (80 MHz) of **8a**.



Figure II.4 <sup>1</sup>H NMR spectrum (90 MHz) of 8d.

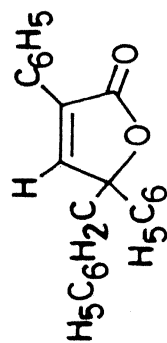
Similarly, the structures of 13a-d were also established on the basis of analytical data and spectral evidence. The IR spectra of all these compounds, for example, showed a sharp carbonyl absorption band at  $1750\text{ cm}^{-1}$ , which is characteristic of five-membered  $\alpha,\beta$ -unsaturated lactones. In addition, the  $^1\text{H}$  NMR spectra of 13a-c showed a singlet at  $\delta\text{ 3.3-3.6}$  (2 H), assigned to the benzylic protons at the C-5 position of the 2(5H)-furanone. The vinylic and aromatic protons appeared as a multiplet centred around  $\delta\text{ 7.2-7.5}$  in each case. The  $^1\text{H}$  NMR spectrum of a representative example, 13a is given in Figure II.5. The  $^1\text{H}$  NMR spectrum of 13d (Figure II.6), however, was slightly different from that of its analogues. In this case, the multiplet pattern seen at  $\delta\text{ 3.2-3.4}$  is resolved into a singlet at  $\delta\text{ 3.35}$  (2 H), assigned to the C-3 benzylic protons and a quartet at  $\delta\text{ 3.28}$  (2 H,  $J = 14\text{ Hz}$ ), which is assigned to the C-5 benzylic protons. The observed geminal coupling of the protons may be due to restricted rotation around the C-C bond or due to the asymmetry of the C-5 carbon to which the benzyl group is attached. The aromatic and vinylic protons in this case appeared as a multiplet centred around  $\delta\text{ 7.15}$ .

### II.3.3 Thermal Transformations of 2(3H)-Furanones 2a-d.

Thermolysis of 2a in a sealed tube at  $250^\circ\text{C}$  for 2 h gave

aromatic and vinylic

7.35



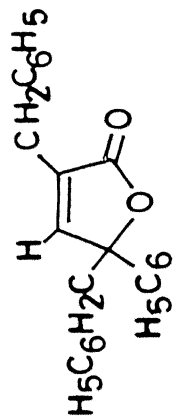
13a

-CH<sub>2</sub>-  
3.4

TMS

← PPM (δ)

Figure II.5 <sup>1</sup>H NMR spectrum (90MHz) of 13a.



**13d**

aromatic and  
vinyl

7.15

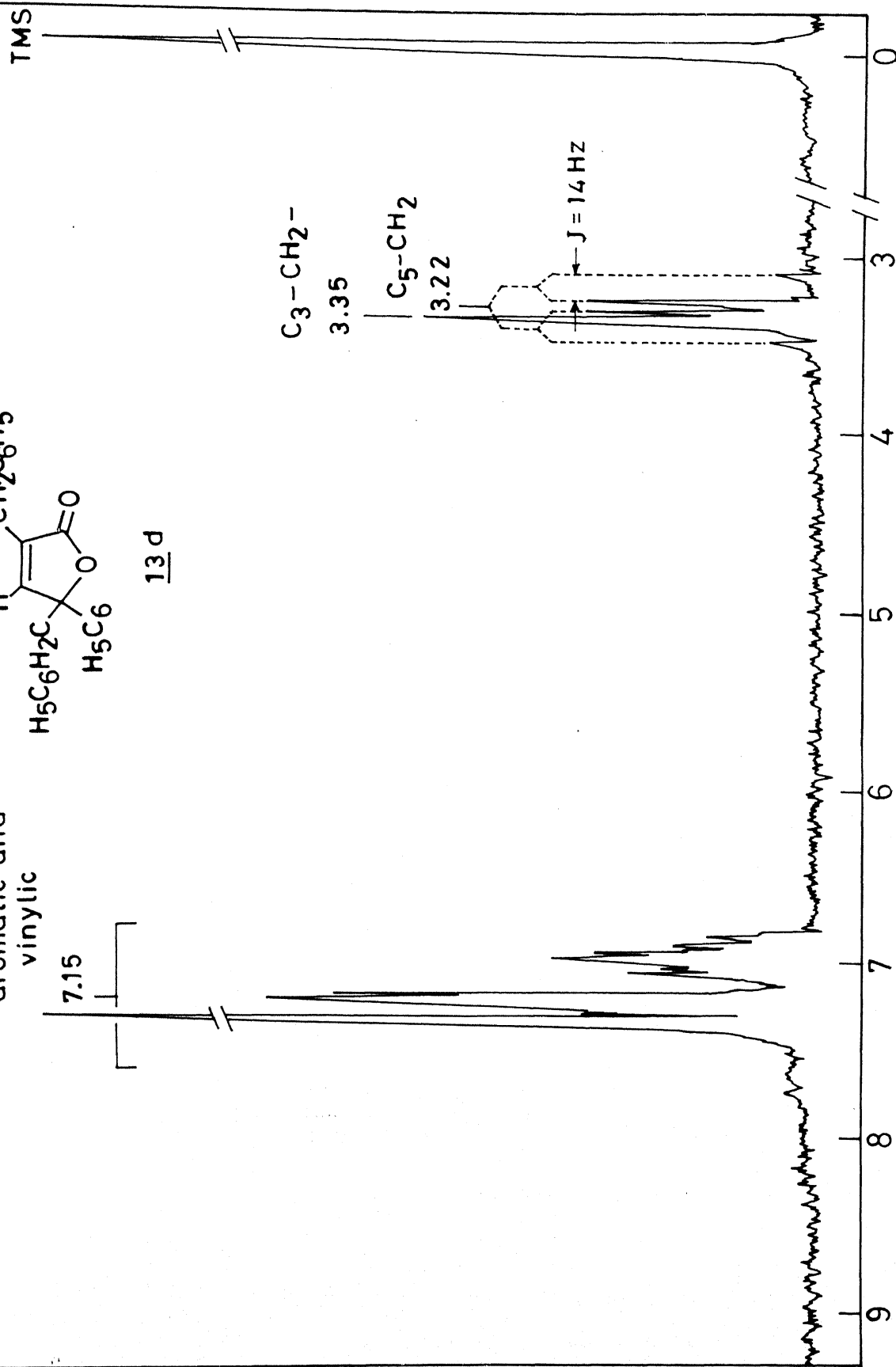


Figure II.6  $^1\text{H}$  NMR spectrum (90 MHz) of **13d**.

the isomeric 2(5H)-furanone 13a, in a 60% yield. Similarly, the thermolysis of 2b-d, under analogous conditions, gave the corresponding 2(5H)-furanones 13b-d, in 70-80% yields.

The formation of the rearranged products 13a-d in the thermolysis of 2a-d may be via a thermal [1,3]-sigmatropic shift with inversion of configuration at the migrating centre<sup>6</sup> or through a radical pathway involving the formation of the furanoxo and benzyl radicals, followed by coupling of these radicals at the C-5 position. This latter pathway, however, may not be very likely since products such as 14a-d that could arise through the coupling of similar radicals, could not be isolated from these reactions.

II.3.4 Laser Flash Photolysis Studies.<sup>12</sup> Photoinduced Electron-Transfer Reactions. Very often, organic photo-reactions leading to isomerization,<sup>13</sup> rearrangement/fragmentation,<sup>14</sup> small molecule extrusion etc., occur as effectively under electron-transfer photosensitization as under direct irradiation. Characterization of the intermediates, namely, exciplexes, ion pairs and radical ions, involved in photo-transformations under photoinduced electron-transfer reaction is critically important for understanding the related photochemical reaction mechanisms. Thus, we have examined the behaviour of the 2(3H)-furanones 2a-c and the bis(benzofuranones) 18a-d under electron-transfer photosensitization

by cyanoaromatics, based on nanosecond laser flash photolysis and steady-state fluorescence quenching. 1,4-Dicyanophthalene (DCN) and 9,10-dicyanoanthracene (DCA) have been used as the sensitizers, which act as singlet excited state acceptors. In addition to measuring fluorescence quenching rate constants and quantum efficiencies of radical ion formation, kinetic studies have also been carried out that establish the fragmentation of radical cations from the 2(3H)-furanones under study, thereby producing furanoxo radicals on a nanosecond time scale. For the purpose of identification, the furanoxo radicals have also been produced by hydrogen abstraction by photogenerated tert-butoxy radical from several appropriate substrates (1a-c and 22a) and also by direct photolysis of 3-benzoyl-3,5-diphenyl-2(3H)-furanone (15).

a) Steady-State Fluorescence Quenching. In acetonitrile solution, the 2(3H)-furanones and bis(benzofuranones) under study, quench the fluorescence of DCN and DCA to variable degrees. The Stern-Volmer quenching constants ( $K_{SV}^F$ ) for these processes were obtained from linear plots based on the equation (1),

$$\frac{I_o^F}{I^F} = 1 + K_{SV}^F [Q] \quad (1)$$

where  $I_o^F$  and  $I^F$  are steady-state fluorescence intensities of the sensitizer (DCN or DCA) in the absence and in the presence of a quencher (Q), respectively. The fluorescence intensities were monitored at or near the wavelength maxima of the sensitizer (380 nm for DCN and 438 nm for DCA). The related quenching rate constants  $k_q^{SS}$  were calculated from equation (2),

$$k_q^{SS} = \frac{K_{SV}^F}{\tau_F} \quad (2)$$

where  $\tau_F$  is the fluorescence lifetime of the sensitizer. The  $K_{SV}^F$  and  $k_q^{SS}$  data are presented in Table II.1.

b) Transient Absorption Spectra of Radicals and Radical Ions. The transient absorption phenomena observed upon 337.1 nm laser flash photolysis of DCN in the presence of 2(3H)-furanones 2a-c show closely resembling behaviour. The transient absorption spectra due to 2a taken at three different time intervals, following the laser flash excitation, are shown as plots A-C in Figure II.7. A close view of the spectra illustrate the growth of transient absorption at 350-380 nm which is concomitant with a decay process seen at 600-750 nm. This growth and concomitant decay process indicate that the radical cations of these substrates undergo further transformation on a nanosecond to microsecond time

Table II.1 Data Concerning DCN and DCA Singlet Quenching by 2(3H)-Furanones and Bis(benzofuranones) and Spectral/Kinetic Behaviour of Radical Cations in Acetonitrile

Quencher	$\tau_{Fns}$	Substrate	$K_{SV}^F$ <sup>a</sup> $M^{-1}$	$10^{10} k_{ss}$ $M^{-1}s^{-1}$	$\delta_{ion}$ <sup>b</sup>	$\lambda_{max}^{S+}$ <sup>c</sup> nm	$\tau_{S+}$ <sup>d</sup> $\mu s$
DCN	9.5	<u>2a</u>	129	1.4	0.5	390	0.22
		<u>2b</u>	161	1.7	0.3	390	0.18
		<u>2c</u>	168	1.8	0.4	440	2.90
		<u>18a</u>	~20	~0.2	-	-	-
		<u>18b</u>	117	1.2	0.2	490	1.00
		<u>18c</u>	106	1.1	0.2	490	0.90
		<u>18d</u>	71	0.75	0.3	490	0.90
DCA	15.7	<u>2a</u>	49	0.31	-	-	-
		<u>2c</u>	169	1.10	0.2	440	-

$\pm 15\%$

$\pm 25\%$

$\pm 5$  nm; maxima at 600-750 nm or 300-330 nm are not included

For decay by first-order kinetics (where applicable) in aerated acetonitrile



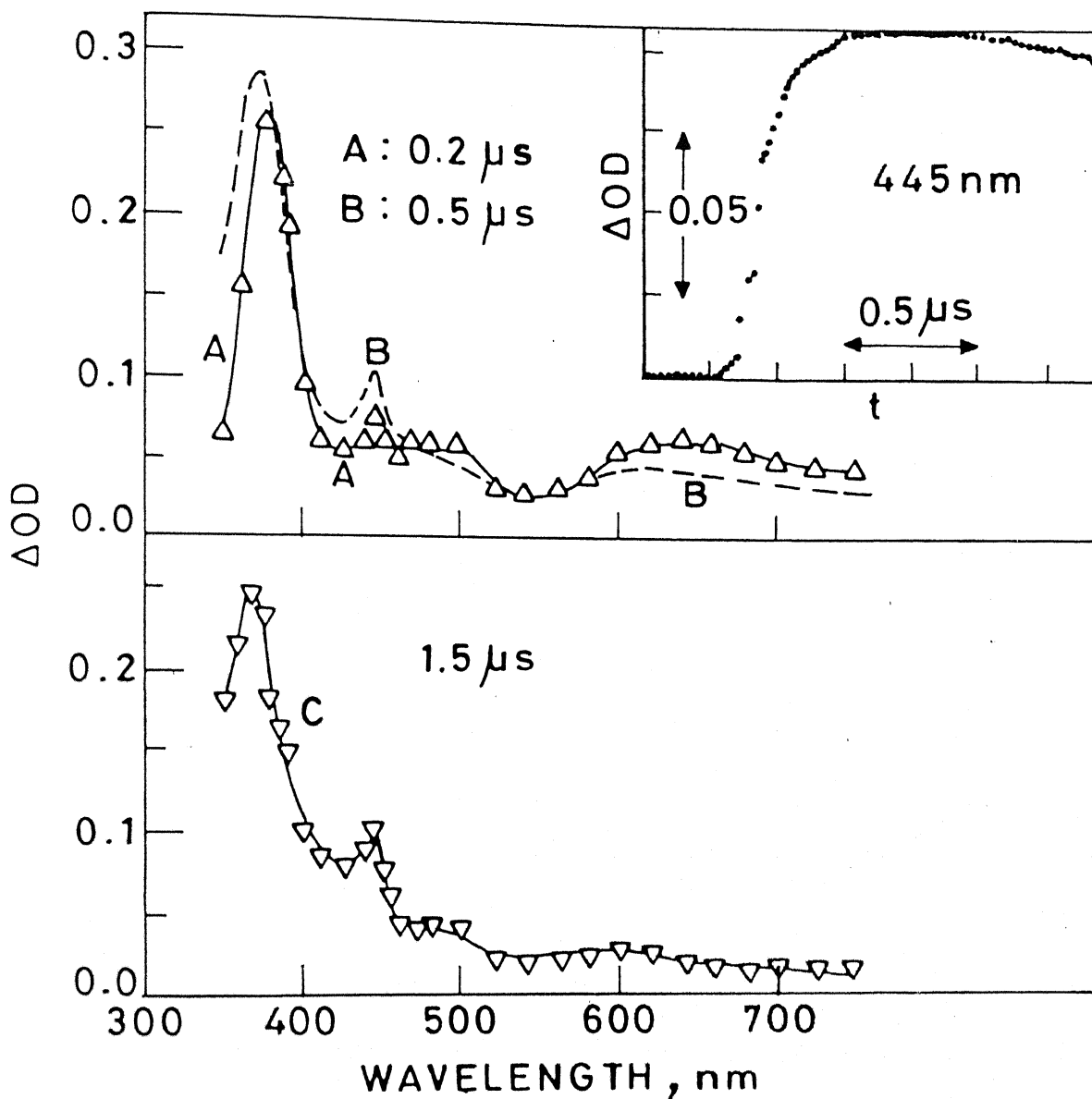


Figure II.7 Transient absorption spectra observed upon 337.1 nm laser flash photolysis of DCN in the presence of 2a in deoxygenated acetonitrile at (A) 0.2, (B) 0.5 and (C) 1.5  $\mu s$  following laser flash. Inset shows the growth of transient absorption at 445 nm.

scale. We believe that the transformation taking place is a fragmentation at the C-3 position of the radical cation to generate the corresponding furanoxo radicals and benzyl cation. The sequence of events taking place in these reactions is given in Scheme II.4.

The inset in Figure II.7 shows the growth of transient absorption at 445 nm in this experiment. As is evident from this plot, the growth process indicating the furanoxo radical formation reaches a level of saturation at  $\sim 1.25 \mu\text{s}$  after the laser flash and it starts decaying thereafter. So, one can safely assume that the transient absorption spectrum taken at  $5 \mu\text{s}$ , following the laser flash (Figure II.8 (A)), is primarily due to the furanoxo radical 11a.

In an attempt to prove that the structured absorption spectrum in Figure II.8 (A) observed at  $\leq 5 \mu\text{s}$  following the laser flash photolysis of DCN in the presence of 2a in aerated acetonitrile is due to the furanoxo radical 11a, we have tried to generate this radical through hydrogen abstraction from the 2(5H)-furanone 1a. Laser photolysis<sup>16</sup> (337.1 nm) of di-tert-butyl peroxide in a 2:1 mixture (v/v) of the peroxide and benzene produces tert-butoxy radical, which can react with the 2(5H)-furanone 1a to generate the furanoxo radical 11a on microsecond time scales. The sequence of

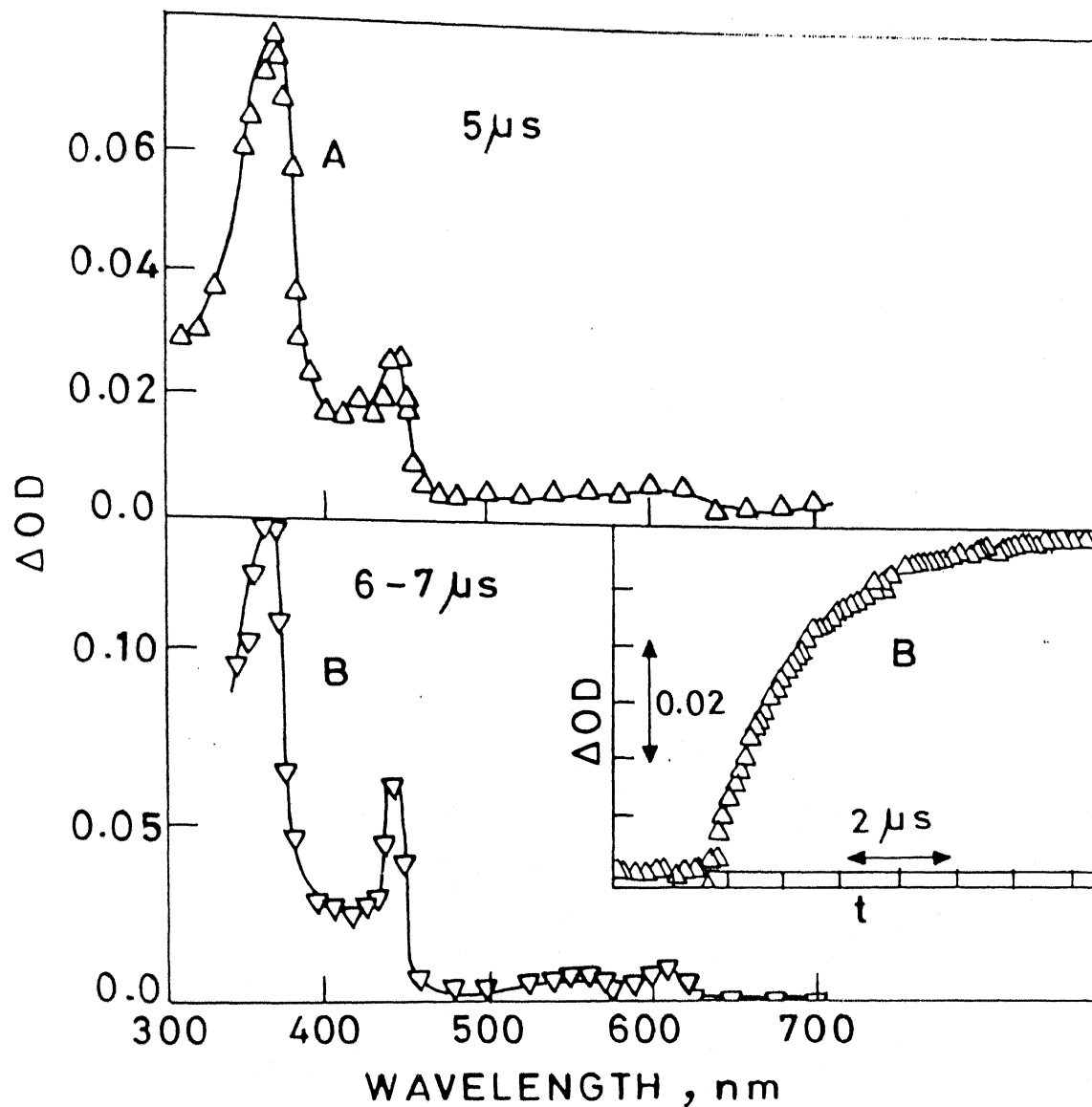


Figure II.8 (A) Transient absorption spectrum observed upon 337.1 nm laser flash photolysis of DCN in the presence of 2a at  $5 \mu s$  and (B) Transient absorption spectrum due to furanoxo radicals at  $6-7 \mu s$  following 337.1 nm laser flash photolysis of t-BuOOBu-t in the presence of 1a. Inset shows kinetic trace at 445-460 nm.

reactions are indicated in Scheme II.6. The related transient spectrum and growth kinetics in the reaction of 1a is shown in Figure II.8 (B). The inset shows growth of transient absorption due to furanoxo radicals at 445-460 nm. A comparison of the spectra (A) and (B) in Figure II.8 indicates that they are due to the same species, thereby proving our assumption.

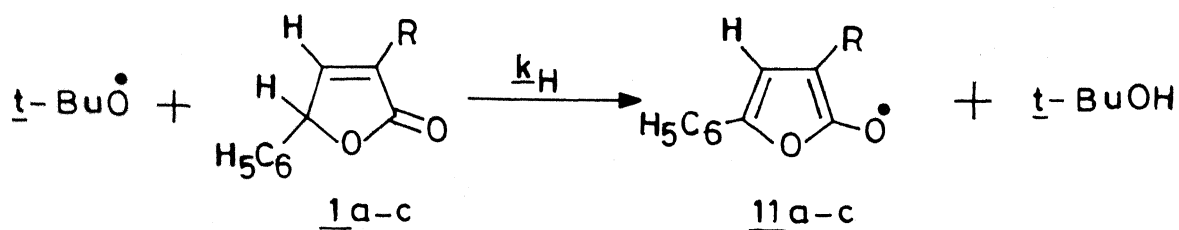
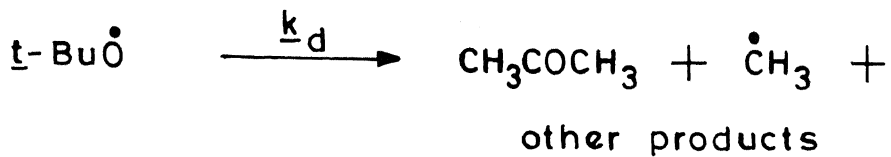
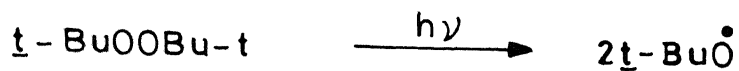
Under photoinduced electron-transfer by  $^1\text{DCN}^*$ , furanones 2b,c also showed transient absorption spectra with structures and locations similar to that of 2a. The corresponding furanoxo radicals have also been generated through hydrogen abstraction from the respective 2(5H)-furanones 1b,c. The transient absorption spectrum obtained in the case of 1b is given in Figure II.9 (A). Based on the equations given in Scheme II.6, the pseudo-first-order rate constant ( $k_{\text{obsd}}$ ) for the growth of transient absorption due to furanoxo radical is given by the following expression,

$$k_{\text{obsd}} = k_d + k_H [S] \quad (3)$$

where  $[S]$  represents the substrate concentration.

Linear plots of  $k_{\text{obsd}}$  vs.  $[S]$  were used to determine  $k_H$  (as slopes). Also, comparison of the absorbance changes due to the furanoxo radicals with those due to diphenylhydroxymethyl

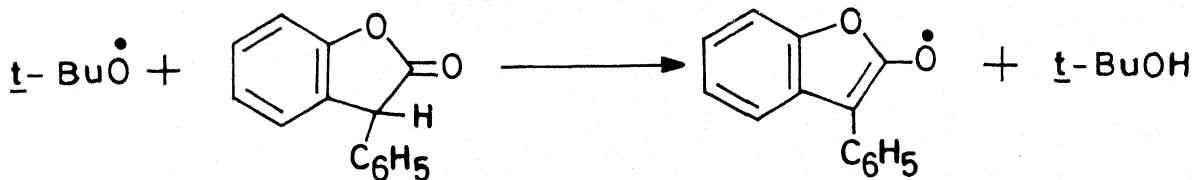
## Scheme II.6



a, R = C<sub>6</sub>H<sub>5</sub>

b, R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>

c, R = p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>



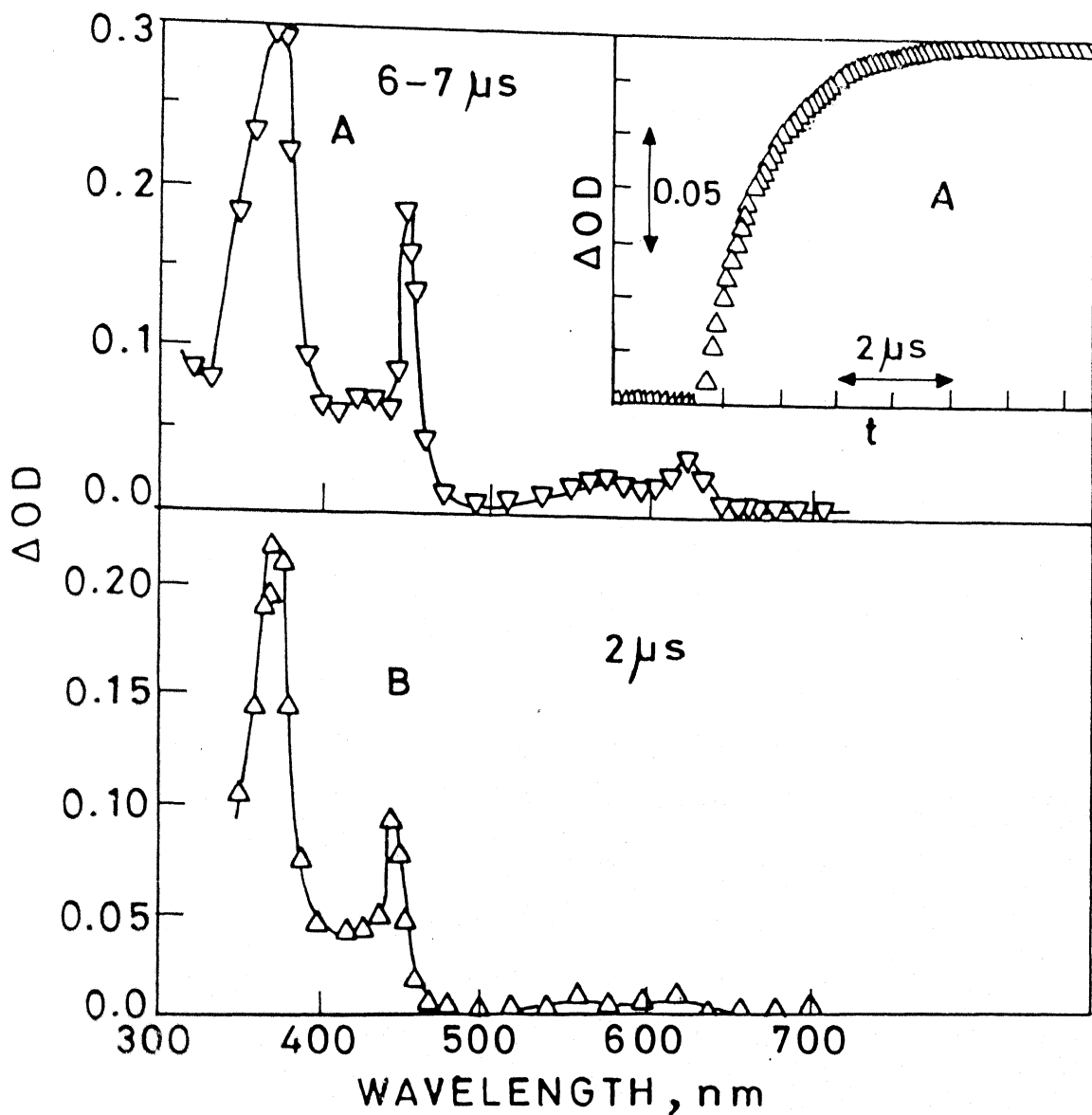


Figure II.9 Transient absorption spectra due to furanoxo radicals: (A) at 6-7  $\mu$ s following 337.1 nm laser flash photolysis of t-BuOOBu-t in the presence of 1b and (B) at 2  $\mu$ s following 337.1 nm laser flash photolysis of 15. Inset shows kinetic traces at 445-460 nm.

radical ( $\epsilon_{\text{max}} = 3.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 545 nm)<sup>17</sup> obtained from diphenylmethanol as well as p-methoxyphenoxy radical ( $\epsilon_{\text{max}} = 4.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 405 nm)<sup>16b</sup> enabled us to determine the extinction coefficients of the furanoxo radicals. Data concerning hydrogen abstraction kinetics and furanoxo radical spectra are summarized in Table II.2.

Preliminary investigations<sup>9</sup> showed that the furanoxo radical 11a can also be produced by acetophenone or benzophenone sensitized irradiation of 2a. Laser flash photolysis (337.1 nm) of a solution of 2a in benzene, containing benzophenone, produced the triplet of 2a, which underwent cleavage at the C-3 position to produce the furanoxo radical 11a and benzyl radical 12. We have observed that the direct irradiation of the benzoyl derivative 15 provides yet another method for the generation of the furanoxo radical 11a. The formation of 11a in this case, involving the 337.1 nm laser flash photolysis of a benzene solution of 15, takes place within the laser pulse ( $\sim 8$  ns). This suggests that if the fragmentation of 15 to 11a under direct excitation involves the intermediacy of the triplet of 15, then the latter is very short lived ( $< 5$  ns). Using benzophenone triplet formation for actinometry, the yield of radical formation under direct excitation of 15 is estimated at  $0.55 \pm 0.15$  in degassed benzene. This value remains

Table II.2 Spectral and Kinetic Properties of Furanoxyl Radicals in 1:2 Benzene-Di-tert-butyl Peroxide (v/v)

Sub- strate	$10^7 k_H^{\cdot a}$ $M^{-1} s^{-1}$	$\lambda_{max}^{\cdot b}$ nm	$10^3 \epsilon_{max}^{\cdot c}$ $M^{-1} cm^{-1}$	$10^8 k_{2,d}^{\cdot a}$ $M^{-1} s^{-1}$
<u>1a</u>	2.0	370 445 610 <sup>d</sup>	16.0 7.2 1.1	6.2
<u>1b</u>	1.8	370 450 620 <sup>d</sup>	15.0 7.8 1.6	6.2
<u>1c</u>	2.0	370 460 630 <sup>d</sup>	12.0 10.0 2.4	6.2
<u>22a</u>	2.0	330 600	14.0 1.2	8.1

a  $\pm 15\%$

b  $\pm 5$  nm

c  $\pm 20\%$

d A minor vibronic peak belonging to the long wavelength band system is located at 550-570 nm.



unchanged upon air-saturation. The transient absorption spectrum obtained in this case is shown in Figure II.9 (B).

The radical cations from bis(benzofuranones) 18b-d produced by electron-transfer to  $^1\text{DCN}^*$  also behave similarly in terms of their further transformations. For example, the transient absorption spectrum of 18c (Figure II.10) shows growth of transient absorption at 310-330 nm and concomitant decay at 450-700 nm, both occurring within a few microseconds, following the laser flash. This is ascribed to the fragmentation of the radical cation across the  $\text{C}_3-\text{C}_3$  bond, giving rise to benzofuranoxo radical (21) and benzofuranyl cation (20) (Scheme II.5). The inset in Figure II.10 shows the growth of this process which reaches a level of saturation at  $\sim 2.5 \mu\text{s}$ , following the laser flash. Thus, we believe that the spectrum taken at  $3 \mu\text{s}$ , following the laser flash in this case (Figure II.11 (A)) is primarily due to the benzofuranoxo radical 21c. This assignment has been further confirmed by generating similar radicals through hydrogen abstraction by photogenerated tert-butoxy radical from the benzofuranone 22a (Scheme II.6). The transient absorption spectrum obtained in this reaction (Figure II.11 (B)) is very much similar to the spectrum obtained at  $3 \mu\text{s}$ , following the laser flash photolysis of 18c in

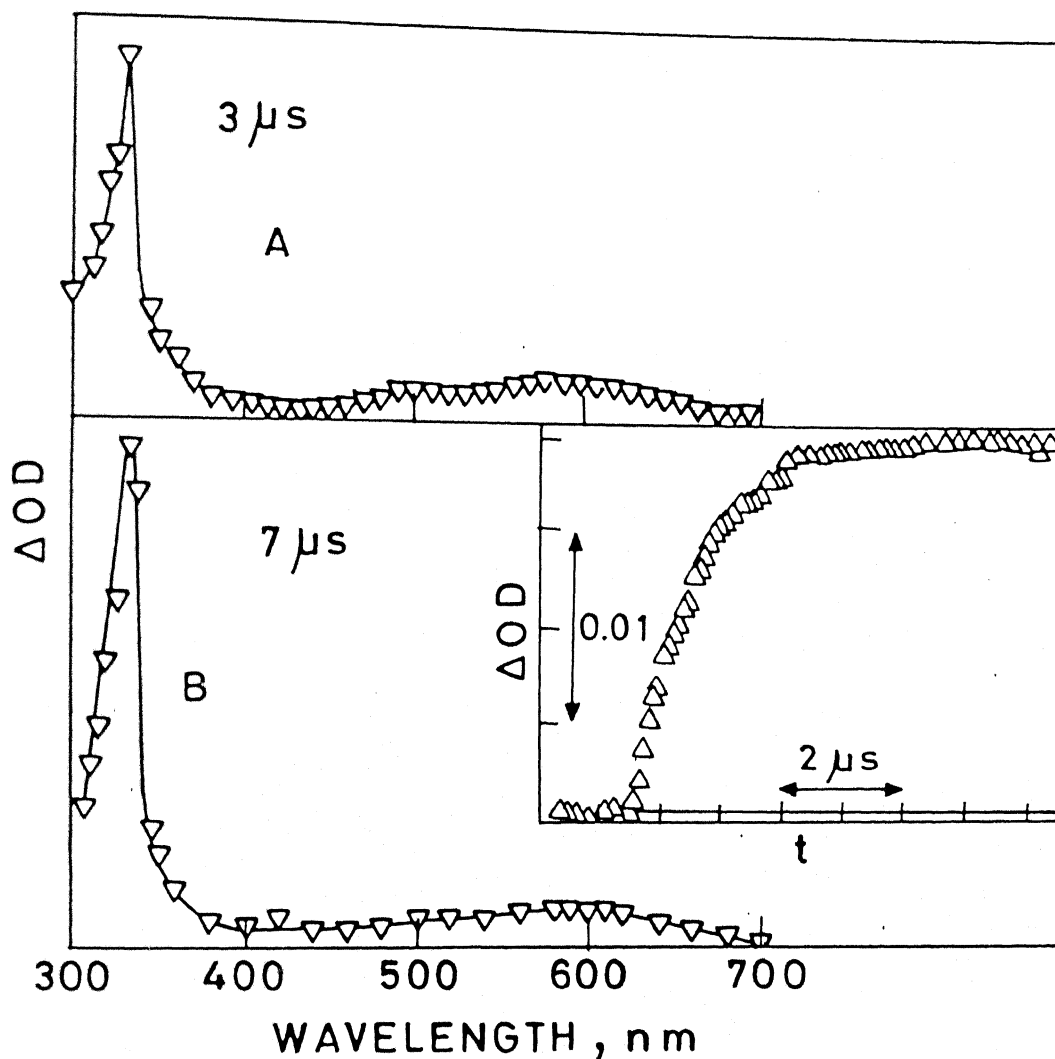


Figure II.11 Transient absorption spectra due to benzo-furanoxo radicals: (A) at 3  $\mu$ s following the laser flash photolysis of DCN in the presence of 18c and (B) at 7  $\mu$ s following the laser flash photolysis of t-BuOOBu-t in the presence of 22a. Inset shows growth of the radical at 610 nm.

presence of DCN (Figure II.11 (A)). Furthermore, it has been shown earlier<sup>1</sup> that direct irradiation of bis(benzofuranones) 18a-d by 248 nm laser pulse results in C<sub>3</sub>-C<sub>3</sub> bond cleavage, giving benzofuranoxo radicals; their spectra are identical with those observed for 18b-d under DCN sensitization in the present study.

c) Decay and Quenching of Radicals and Radical Cations.

The decay of radical cations from 18b-d at 490 nm could be fitted approximately into first-order kinetics with lifetimes ( $\tau_{S^+}$ ) close to 1  $\mu$ s. Comparatively, the first-order decay of radical cations from 2a,b (at 700 nm) were faster ( $\tau_{S^+} \sim 0.2 \mu$ s). In the case of 2c,  $\tau_{S^+}$  was measured from the first-order growth of the furanoxo radical 11c at 370 nm. The  $\tau_{S^+}$  data are presented in Table II.1.

The quenching effects of several reagents, namely, water, methanol and Br<sup>-</sup>, which are expected to act as nucleophilic quenchers for radical cations, were studied with 2a and 18c as the substrates. The pseudo-first-order rate constants ( $k_{\text{obsd}}$ ) for S<sup>+</sup> decay (monitored at 700 nm for 2a and 490 nm for 18c) were measured as functions of quencher concentrations ([Q]). The slopes of the linear plots of  $k_{\text{obsd}}$  vs. [Q] gave the quenching rate constant  $k_q^{S^+}$ . The data are presented in Table II.3.

Table II.3 Rate Constants for the Quenching of Radical Cations in Acetonitrile

Substrate	Monitoring Wavelength, nm	$k_q^{S^+}, M^{-1} s^{-1} \text{ } ^a$		
		H <sub>2</sub> O	MeOH	Br <sup>-</sup> <sup>b</sup>
<u>2a</u>	700	$3.2 \times 10^6$	$3.7 \times 10^6$	$2.0 \times 10^{10}$
<u>18c</u>	490	$7.4 \times 10^5$	$3.9 \times 10^6$	$2.0 \times 10^{10}$

a  $\pm 20\%$

b Added as tetra-n-propylammonium bromide

The long-lived furanoxo radicals derived from 1a-c, 15 and 22a decay exclusively by second-order equal concentration kinetics. From appropriate fits of kinetic traces over 70-80  $\mu$ s (corresponding to 50-70% decay), we obtained the second-order rate constants ( $k_{2,d}$ ) for decay in 1:2 benzene-di-tert-butyl peroxide. Linear plots of the reciprocal of absorbance against time gave  $k_{2,d}/(\epsilon \cdot l)$  as slopes, where ' $\epsilon$ ' is the extinction coefficient of the radical at the monitoring wavelength and ' $l$ ' is the pathlength of the cell (0.2 cm). The  $\epsilon$  data in Table II.2 were used in computing  $k_{2,d}$ . Note that  $k_{2,d}$ 's (Table II.2) are all smaller than the diffusion controlled rate constant by about one order of magnitude. Under air-saturation, the decay of the radicals become slightly enhanced, but remains predominantly second-order in nature. Approximate fits of kinetic traces under air-saturation into second-order equal concentration kinetics gave  $k_{2,d}$  values 30-40% higher than those under deoxygenated conditions.

d) Efficiency of Charge Separation. The efficiency of photoinduced charge separation was estimated in terms of the fraction ( $\delta_{ion}$ ) of sensitizer singlet quenching events that result in radical ions. The computation of  $\delta_{ion}$  was based on absorbance changes due to radical anions of DCN and DCA monitored at 390 or 705 nm, respectively, and the contributions

of radical cations (or radicals) were corrected for by using absorbance changes due to them, measured in air-saturated solutions. With DCN as the sensitizer ( $\lambda_{\text{ex}} = 425 \text{ nm}$ ), formation of thiocoumarin triplet in an optically matched benzene solution ( $\phi_T = 1$ ,  $\epsilon_{\text{max}}^T = 8.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  at 485 nm)<sup>18</sup> was used for actinometry. The data regarding  $\delta_{\text{ion}}$  are given in Table II.1. As is evident from Table II.1, the efficiencies of net electron-transfer in the course of quenching process are modest (0.2-0.5). There is no indication of a fast, electron-transfer-induced homolytic C-C bond cleavage to benzyl and furanoxo radicals in the case of 2a-c or to two benzofuranoxo radicals in the case of 18b-d.

Discussion. a) Direct Irradiations. The formation of the various photoproducts in the direct irradiation of the 2(3H)-furanones 2a-d and 9 in benzene and methanol could be understood in terms of the pathway shown in Scheme II.2. Initial excitation of the furanones lead to the corresponding singlet excited states which, in turn, undergo decarbonylation to give the intermediate  $\alpha,\beta$ -unsaturated ketones 4a-d. These  $\alpha,\beta$ -unsaturated ketones 4a-d, having a methylene group  $\gamma$ - to the carbonyl functionality, can undergo  $\gamma$ -hydrogen abstraction photochemically to produce the enol intermediates 5a-d, which in turn, can tautomerize to the stable  $\beta,\gamma$ -unsaturated ketones

8a-d. Alternatively, the enol derivatives 5a-c can cyclize to the dihydrofuran derivatives 6a-c. Further transformation of the dihydrofurans under the conditions of workup leads to the furan derivatives 7a-c. Similar photochemical isomerizations of  $\alpha,\beta$ -unsaturated ketones to  $\beta,\gamma$ -unsaturated ketones and related products, through  $\gamma$ -hydrogen abstraction, is well documented in the literature.<sup>19</sup> It is, however, not very clear as to why the corresponding furan derivative is not formed in the case of 2d.

b) Triplet Sensitization. Formation of the rearrangement products 13a-d, as well as the bisfuranones 14a-c in the acetophenone sensitized irradiations of 2a-d can be explained as occurring through the pathway shown in Scheme II.3. As indicated by our preliminary studies,<sup>9</sup> the triplets of 2a-d produced by sensitization, undergo cleavage at the C-3 position to give benzyl radical (12) and furanoxo radicals 11a-d. Recombination of these radicals lead to the formation of the starting materials 2a-d or the rearranged 2(5H)-furanones 13a-d. Alternatively, the furanoxo radicals 11a-c can undergo dimerization to give the bisfuranones 14a-c. Under these conditions, one would also expect the formation of dibenzyl by the dimerization of two benzyl radicals. However, under our experimental conditions we could not isolate any of this product.

The formation of the bisfuranone 14a, in the direct, as well as, sensitized irradiations of 15, also could be understood as occurring through a similar pathway (Scheme II.3), involving cleavage at the C-3 carbon to produce benzoyl radical (16) and furanoxo radical 11a. Since this fragmentation process occurs very fast ( $\sim 8$  ns), we cannot speculate on the exact nature of the fragmenting species. In this case also one would expect the formation of benzil by the coupling of two benzoyl radicals. However, no benzil could be isolated from these reactions.

c) Electron-Transfer Reactions. Schemes II.4 and II.5 indicate the formation of the products in the photoinduced electron-transfer reactions of 2a,b and 18b,c, respectively. The singlet excited states of DCN or DCA accept an electron from these substrates in their ground state, thereby producing the substrate radical cations, which in turn undergo fragmentation. In the case of the bis(benzofuranones), the cation thus generated (20), may be reacting with  $\text{DCN}^-$  to give the radical 21 and DCN. Further reactions of the radicals as in the earlier cases lead to the observed products in these reactions.

The facile fragmentation of radical cations in these reactions is reminiscent of similar behaviour, previously



reported for phenyl glycopyranosides.<sup>20</sup> The radical cations from the latter undergo transformation to phenoxy radicals and glycopyranoside-related carbonium ions. Interestingly, the kinetics of fragmentation is much slower for 2c, relative to 2a and 2b (see  $\tau_{S^+}$  data in Table II.1). A reasonable explanation for this difference is that the oxidation potential of 2c is lower, compared to 2a,b (i.e., the corresponding radical cation is more stable) and thus the free energy change associated with intramolecular electron-transfer causing C-C bond cleavage is less negative in the case of 2c.

#### II.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were recorded on a Mel-Temp apparatus. The IR spectra were recorded on a Perkin-Elmer Model 377 or Model 580 infrared spectrometers. The electronic spectra were recorded on Beckman DB, Cary 17D, Cary 219 or Shimadzu UV-190 spectrophotometers. The  $^1\text{H}$  NMR traces were recorded on Varian A-60, EM-390 or Bruker WP-80 spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Irradiations were carried out in a

Srinivasan-Griffin-Rayonet photochemical reactor (RPR 3000 or 3500 Å) or using a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketed immersion well.

II.4.1 Starting Materials. 2(3H)-Furanones 9, mp 225-226 °C<sup>1</sup> and 15, mp 185-186 °C<sup>10</sup> and the bis(benzofuranones) 18b, mp 201-202 °C<sup>8</sup> and 18c, mp 170-171 °C<sup>8</sup> were prepared by reported procedures. Solvents such as benzene, methanol and acetonitrile used for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

II.4.2 Preparation of 2(3H)-Furanones 2a-d. A general procedure was to stir an equimolar mixture of the appropriate furanones 1a-c<sup>21</sup> or 3<sup>22</sup> and sodium hydride in dry tetrahydrofuran (THF) at 50-60 °C, till the solution became clear yellow. The mixture was then cooled to 0-5 °C and an equivalent amount of benzyl benzenesulfonate was added gradually. After stirring the mixture at 15-20 °C for 20 h, the precipitated sodium salt was filtered off and washed with ether. The combined ether-THF filtrate was evaporated under vacuum and the product was recrystallized from suitable solvents.

3-Benzyl-3,5-diphenyl-2(3H)-furanone (2a). 2a was obtained in nearly quantitative yield, mp 148-149 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3120, 3080, 3060, 3040, 2990 (CH), 1780 (C=O), 1650 and 1595 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 220 nm ( $\epsilon$ , 14,100), 253 (sh, 8,200), 260 (sh, 10,200), 265 (11,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.55 (s, 2 H, methylene), 6.27 (s, 1 H, vinylic) and 7.5 (m, 15 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 84.92; H, 5.37.

3-Benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b).

2b was obtained in a 62% yield, mp 164-165  $^{\circ}\text{C}$ , after recrystallization from ethanol.

IR spectrum  $\nu_{\max}$  (KBr): 3110, 3080, 3060, 3025, 2920, 2850 (CH), 1780 (C=O), 1650 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 251 nm ( $\epsilon$ , 9,400), 268 (13,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.35 (s, 3 H, methyl), 3.43 (s, 2 H, methylene), 6.07 (s, 1 H, vinylic) and 7.3 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_2$ : C, 84.70; H, 5.88. Found: C, 84.77; H, 5.82.

3-Benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone

(2c). 2c was obtained in a 70% yield, mp 138-139 °C, after recrystallization from ethanol.

IR spectrum  $\nu_{\max}$  (KBr): 3120, 3060, 3025, 2920, 2840 (CH), 1780 (C=O), 1650 and 1605 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 238 nm ( $\epsilon$ , 12,100), 266 (21,000).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.33 (s, 2 H, methylene), 3.75 (s, 3 H, methoxy), 6.0 (s, 1 H, vinylic) and 7.2 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_3$ : C, 80.90; H, 5.62. Found: C, 81.07; H, 5.28.

3,3-Dibenzyl-5-phenyl-2(3H)-furanone (2d). 2d was obtained in a 60% yield,<sup>23</sup> mp 176-177 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3100, 3070, 3050, 3020, 2920 (CH), 1770 (C=O), 1650 and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 262 nm ( $\epsilon$ , 14,100), 267 (sh, 13,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.1 (q, 4 H,  $J = 14$  Hz; methylene, protons are inequivalent due to restricted rotation), 5.7 (s, 1 H, vinylic) and 7.23 (m, 15 H, aromatic).

Anal. Calcd for  $C_{24}H_{20}O_2$ : C, 84.70; H, 5.88. Found: C, 84.35; H, 5.80.

II.4.3 Photolysis of 3-Benzyl-3,5-diphenyl-2(3H)-furanone (2a). A solution of 2a (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 0.5 h (RPR, 3000 Å). The experiment was repeated several times to photolyse, in all, 350 mg (1.07 mmol) of 2a. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution of the column with petroleum ether gave 25 mg (8%) of 7a, mp 92-93 °C (mixture melting point),<sup>11</sup> after recrystallization from methanol. Further elution with a mixture (3:7) of benzene and petroleum ether gave 121 mg (34%) of the unchanged starting material 2a, mp 148-149 °C (mixture melting point), after recrystallization from methanol. Continued elution of the column with a mixture (2:3) of benzene and petroleum ether gave 70 mg (20%) of 8a,<sup>24</sup> mp 132-133 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3080, 3050, 3020 (CH), 1684 (C=O), 1595 and 1580 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 223 nm ( $\epsilon$ , 22,100), 244 (23,100).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  4.35 (s, 2 H, methylene), 7.05 (s, 1 H, vinylic) and 7.5 (m, 15 H, aromatic).

Mass spectrum,  $m/e$  (relative intensity): 298 ( $M^+$ , 20), 193 ( $M^+ - \text{COC}_6\text{H}_5$ , 5), 179 ( $M^+ - \text{COC}_6\text{H}_5, - \text{CH}_2$ , 1), 178 ( $M^+ - \text{COC}_6\text{H}_5, - \text{CH}_2, - \text{H}$ , 7) and other peaks.

Anal. Calcd for  $\text{C}_{22}\text{H}_{18}\text{O}$ : C, 88.59; H, 6.04. Found: C, 88.86, H, 5.92.

In a repeat run, a solution of 2a (50 mg, 0.15 mmol) in methanol (150 mL) was irradiated for 0.5 h (RPR, 3000 Å). The experiment was repeated several times to irradiate in all, 250 mg (0.77 mmol) of 2a. Workup as in the earlier case gave 20 mg (9%) of 7a, mp 92-93 °C (mixture melting point), 94 mg (37%) of the unchanged starting material, mp 148-149 °C (mixture melting point) and 60 mg (26%) of 8a, mp 132-133 °C (mixture melting point).

In another experiment, a solution of 2a (200 mg, 0.61 mmol) in benzene (150 mL) containing acetophenone (50 mg, 0.42 mmol) was irradiated for 3 h (RPR, 3500 Å). The solvent was removed under vacuum and the residue was filtered and washed with boiling methanol to yield 40 mg (27%) of 14a, mp 285-288 °C (mixture melting point).<sup>21</sup> The filtrate was concentrated and chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 50 mg (25%) of the unchanged starting material, mp 148-149 °C (mixture melting point), after recrystallization from

methanol. Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 70 mg (35%) of the 2(5H)-furanone 13a, mp 163-164 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3080, 3060, 3020 (CH), 1740 (C=O), 1600 and 1500 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 259 nm ( $\epsilon$ , 21,200), 264 (21,000).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.4 (s, 2 H, methylene) and 7.35 (m, 16 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 85.02; H, 5.45.

In another experiment, a solution of 2a (195 mg, 0.6 mmol) in acetonitrile (150 mL) containing DCN (9 mg, 0.05 mmol) was irradiated for 5.5 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter. Removal of the solvent under vacuum gave a residue, which was filtered and washed with boiling methanol to yield 90 mg (64%) of 14a, mp 285-288 °C (mixture melting point). The filtrate was purified by column chromatography over silica gel to give 50 mg (25%) of the unchanged starting material, mp 148-149 °C (mixture melting point), after recrystallization from methanol.

II.4.4 Photolysis of 3-Benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b). A solution of 2b (50 mg, 0.15 mmol) in benzene (150 mL) was irradiated for 0.5 h (RPR, 3000 Å). The experiment was repeated several times to photolyse, in all, 350 mg (1.05 mmol) of 2b. Removal of the solvent gave a residue which was chromatographed over silica gel. Elution of the column with petroleum ether gave 20 mg (6%) of 7b, mp 126-127 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3040, 3020, 3000, 2910 (CH), 1580 (C=C) and 1140 (C-O)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 240 nm ( $\epsilon$ , 12,400), 266 (17,600).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.4 (s, 3 H, methyl), 6.75 (s, 1 H, vinylic) and 7.45 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}$ : C, 89.03; H, 5.81. Found: C, 88.72; H, 5.50.

Continued elution of the column with a mixture (3:7) of benzene and petroleum ether gave 192 mg (54%) of the unchanged starting material (2b), mp 164-165 °C (mixture melting point), after recrystallization from methanol. Further elution with



a mixture (2:3) of benzene and petroleum ether gave 101 mg (31%) of 8b, mp 64-65 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3040, 3020, 2920 (CH), 1680 (C=O), 1595 and 1570 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 220 nm ( $\epsilon$ , 21,700), 250 (21,700).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.4 (s, 3 H, methyl), 4.53 (s, 2 H, methylene), 6.66 (s, 1 H, vinylic) and 7.71 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}$ : C, 88.46; H, 6.41. Found: C, 88.06; H, 6.23.

In a repeat experiment, a solution of 2b (50 mg, 0.15 mmol) in methanol (150 mL) was irradiated for 0.5 h (RPR, 3000 Å). The experiment was repeated several times so as to irradiate, in all, 200 mg (0.6 mmol) of 2b. Removal of the solvent followed by workup, as in the earlier case, gave 24 mg (13%) of 7b, mp 126-127 °C (mixture melting point), 80 mg (40%) of the unchanged starting material (2b), mp 164-165 °C (mixture melting point) and 40 mg (21%) of 8b, mp 64-65 °C (mixture melting point).

Irradiation of 2b (400 mg, 1.17 mmol) in benzene (150 mL) containing acetophenone (60 mg, 0.5 mmol) for 3 h (RPR, 3500 Å)

and removal of the solvent under vacuum gave a solid, which was filtered and washed with boiling methanol to yield 20 mg (7%) of the bisfuranone 14b, mp 258-260 °C (mixture melting point). The filtrate was concentrated and chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 100 mg (25%) of the unchanged starting material (2b), mp 164-165 °C (mixture melting point), after recrystallization from methanol. Continued elution of the column with a mixture (1:1) of benzene and petroleum ether gave 200 mg (50%) of 13b, mp 140-141 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3090, 3020, 2920 (CH), 1745 (C=O), 1500 and 1490 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 264 nm ( $\epsilon$ , 9,200), 270 (9,400).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  2.53 (s, 3 H, methyl), 3.60 (s, 2 H, methylene) and 7.48 (m, 15 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_2$ : C, 84.70, H, 5.88. Found: C, 84.30; H, 5.42.

In a repeat experiment, a solution of 2b (204 mg, 0.6 mmol) in acetonitrile (150 mL) containing DCN (9 mg, 0.05 mmol) was irradiated for 5.5 h (RPR, 3500 Å), using a 2 mM

naphthalene solution in benzene as filter. Workup of the reaction mixture as in the case of 2a gave 100 mg (66%) of the bisfuranone 14b, mp 258-260 °C (mixture melting point), and 26 mg (12%) of the unchanged starting material (2b), mp 164-165 °C (mixture melting point), after recrystallization from methanol.

II.4.5 Photolysis of 3-Benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone (2c). A solution of 2c (50 mg, 0.14 mmol) in benzene (150 mL) was irradiated for 0.5 h (RPR, 3000 Å). The experiment was repeated three times more so as to irradiate, in all, 200 mg (0.56 mmol) of 2c. Removal of the solvent under vacuum gave a residue, which was chromatographed over silica gel. Elution of the column with petroleum ether gave 15 mg (8%) of 7c, mp 120-121 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3100, 3040, 2950 (CH), 1600 (C=C), 1250 and 1020 (C-O)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 246 nm ( $\epsilon$ , 11,600), 270 (22,400).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.9 (s, 3 H, methoxy), 6.83 (s, 1 H, vinylic) and 7.5 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_2$ : C, 84.66; H, 5.52. Found: C, 84.50; H, 5.28.

Continued elution of the column with a mixture (3:7) of benzene and petroleum ether gave 100 mg (50%) of the unchanged starting material (2c), mp 138-139 °C (mixture melting point), after recrystallization from methanol. Further elution with a mixture (2:3) of benzene and petroleum ether gave 47 mg (25%) of 8c, mp 112-113 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3080, 3020, 2950, 2900 (CH), 1680 (C=O), 1605 and 1595 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 245 nm ( $\epsilon$ , 54,000), 277 (53,000).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.75 (s, 3 H, methoxy), 4.3 (s, 2 H, methylene), 6.7 (s, 1 H, vinylic) and 7.5 (m, 14 H, aromatic).

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_2$ : C, 84.14; H, 6.1. Found: C, 84.47; H, 5.82.

Irradiation of a solution of 2c (200 mg, 0.56 mmol) in methanol, as in the earlier case, followed by workup gave 20 mg (11%) of 7c, mp 120-121 °C (mixture melting point), 100 mg (50%) of the unchanged starting material (2c), mp 138-139 °C (mixture melting point) and 44 mg (24%) of 8c, mp 112-113 °C (mixture melting point).

In another experiment, a solution of 2c (400 mg, 1.12 mmol) in benzene (150 mL) containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å). Removal of the solvent under vacuum gave a residual solid, which was filtered and washed with boiling methanol to yield 20 mg (6%) of the bisfuranone 14c, mp 230-233 °C (mixture melting point). The filtrate was concentrated and chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 100 mg (25%) of the unchanged starting material (2c), mp 138-139 °C (mixture melting point), after recrystallization from methanol. Continued elution with a mixture (1:1) of benzene and petroleum ether gave 190 mg (47%) of the 2(5H)-furanone 13c, mp 153-154 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3080, 3020, 2950, 2830 (CH), 1740 (C=O), 1605 and 1510 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 281 nm ( $\epsilon$ , 10,500), 296 (sh, 8,800).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.35 (s, 2 H, methylene), 3.75 (s, 3 H, methoxy) and 7.22 (m, 15 H, aromatic and vinylic).

Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_3$ : C, 80.90; H, 5.62. Found: C, 80.68; H, 5.45.

II.4.6 Photolysis of 3,3-Dibenzyl-5-phenyl-2(3H)-furanone (2d). A solution of 2d (340 mg, 1 mmol) in benzene (150 mL) was irradiated for 4 h (RPR, 3000 Å) and worked up by removing the solvent under vacuum and chromatographing the residue over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 250 mg (80%) of 8d, mp ca. 20 °C.

IR spectrum  $\nu_{\text{max}}$  (thin film): 3050, 3020, 2910, 2840 (CH), 1670 (C=O), 1610 and 1595 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 254 nm ( $\epsilon$ , 14,100), 262 (sh, 13,300).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.43 (s, 2 H, methylene), 3.97 (s, 2 H, methylene), 6.73 (s, 1 H, vinylic) and 7.47 (m, 15 H, aromatic).

Mass spectrum, m/e (relative intensity): 312 ( $\text{M}^+$ , 27), 221 ( $\text{M}^+ - \text{CH}_2\text{C}_6\text{H}_5$ , 75), 220 ( $\text{M}^+ - \text{CH}_2\text{C}_6\text{H}_5$ , - H, 6), 207 ( $\text{M}^+ - \text{COC}_6\text{H}_5$ , 3), 193 ( $\text{M}^+ - \text{COC}_6\text{H}_5$ , -  $\text{CH}_2$ , 3), 192 ( $\text{M}^+ - \text{COC}_6\text{H}_5$ , -  $\text{CH}_2$ , - H, 3), 105 ( $\text{C}_6\text{H}_5\text{CO}^+$ , 100), 91 ( $\text{C}_6\text{H}_5\text{CH}_2^+$ , 65) and other peaks.

Anal. Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}$ : C, 88.46; H, 6.41. Found: C, 88.85; H, 6.34.

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 40 mg (12%) of the unchanged

starting material, mp 176-177 °C (mixture melting point), after recrystallization from methanol.

Irradiation of a solution of 2d (340 mg, 1 mmol) in methanol (150 mL) for 4 h (RPR, 3000 Å) and workup as in the earlier case gave 260 mg (83%) of 8d and 50 mg (14%) of the unchanged starting material, mp 176-177 °C (mixture melting point).

In another experiment, a solution of 2d (340 mg, 1 mmol) in benzene (150 mL) containing acetophenone (60 mg, 0.5 mmol) was irradiated for 3 h (RPR, 3500 Å). The reaction mixture was worked up by removal of the solvent under vacuum, followed by chromatographing the residue over silica gel. Elution of the column with a mixture (1:1) of benzene and petroleum ether gave 200 mg (58%) of the unchanged starting material, mp 176-177 °C (mixture melting point), after recrystallization from methanol. Further elution with a mixture (3:2) of benzene and petroleum ether gave 90 mg (23%) of the 2(5H)-furanone 13d, mp 135-136 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3090, 3050, 3020, 2910 (CH), 1740 (C=O) and 1600 (C=C)  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\max}$  (methanol): 258 nm ( $\epsilon$ , 2,100), 263 (sh, 1,700).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ):  $\delta$  3.28 (q, 2 H,  $J = 14$  Hz, C-5 methylene), 3.35 (s, 2 H, C-3 methylene) and 7.15 (m, 16 H, aromatic and vinylic).

Mass spectrum,  $m/e$  (relative intensity): 340 ( $\text{M}^+$ , 3), 249 ( $\text{M}^+ - \text{CH}_2\text{C}_6\text{H}_5$ , 85), 235 ( $\text{M}^+ - \text{CO}$ , -  $\text{C}_6\text{H}_5$ , 1), 205 ( $\text{M}^+ - \text{CH}_2\text{C}_6\text{H}_5$ , -  $\text{CO}_2$ , 4), 105 ( $\text{C}_6\text{H}_5\text{CO}^+$ , 100), 91 ( $\text{C}_6\text{H}_5\text{CH}_2^+$ , 44) and other peaks.

Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{O}_2$ : C, 84.70; H, 5.88. Found: C, 84.31; H, 5.57.

II.4.7 Photolysis of 3-Benzyl-3-phenylphenanthro[9,10-b]-furan-2(3H)-one (9). A solution of 9 (100 mg, 0.25 mmol) in benzene (150 mL) was irradiated for 10 h (RPR, 3000 Å). Removal of the solvent under vacuum gave a residue which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 15 mg (16%) of 10, mp 192-193 °C (lit.<sup>25</sup> mp 193-194 °C), after recrystallization from methanol. Further elution of the column with mixture (2:3) of benzene and petroleum ether gave 45 mg (45%) of the unchanged starting material (9), mp 225-226 °C (mixture melting point), after recrystallization from methanol.

In a repeat experiment, a solution of 9 (100 mg, 0.25 mmol) in methanol (150 mL) was irradiated for 10 h (RPR,



3000 Å). Removal of the solvent and workup as in the earlier case gave 20 mg (21%) of 10, mp 192-193 °C (mixture melting point) and 20 mg (20%) of the unchanged starting material (9), mp 225-226 °C (mixture melting point).

II.4.8 Photolysis of 3-Benzoyl-3,5-diphenyl-2(3H)-furanone (15). A solution of 15 (340 mg, 1 mmol) in benzene (150 mL) was irradiated for 3 h (RPR, 3000 Å). Removal of the solvent gave a residue, which was filtered and washed with methanol to give 170 mg (72%) of the bisfuranone 14a, mp 285-288 °C (mixture melting point).

In a repeat experiment, a solution of 15 (200 mg, 0.59 mmol) in methanol (150 mL) was irradiated for 3 h (RPR, 3000 Å). Removal of the solvent and workup of the reaction mixture as in the earlier case gave 105 mg (75%) of 14a, mp 285-288 °C (mixture melting point).

II.4.9 Photolysis of 5,5'-Dimethyl-3,3'-diphenyl-3,3'-bibenzo[b]furan-2,2'(3H,3'H)-dione (18b). A solution of 18b (224 mg, 0.5 mmol) in acetonitrile (150 mL) containing DCN (20 mg, 0.11 mmol) was irradiated for 1.5 h (RPR, 3500 Å), using a 2 mM naphthalene solution in benzene as filter. The solvent was removed under vacuum and the residue was chromatographed over silica gel. Elution of the column with a mixture (1:4) of benzene and petroleum ether gave 75 mg (33%) of 22b, mp 105-106 °C (mixture melting point),<sup>1</sup> after

recrystallization from methanol. Continued elution with a mixture (2:3) of benzene and petroleum ether gave 18 mg (90% recovery) of DCN, mp 210-211 °C (mixture melting point), after recrystallization from methanol. Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 100 mg (44%) of the unchanged starting material (18b), mp 201-202 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether. Continued elution with benzene gave 50 mg (19%) of 24b, mp 105-106 °C (lit.<sup>1</sup> mp 105-106 °C), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

II.4.10 Photolysis of 6,6'-Dimethyl-3,3'-diphenyl-3,3'-dibenzo[b]furan-2,2'(3H,3'H)-dione (18c). A solution of 18c (224 mg, 0.5 mmol) in acetonitrile (150 mL) containing DCN (20 mg, 0.11 mmol) was irradiated for 1.5 h (RPR, 3500 Å) using a 2 mM solution of naphthalene in benzene as filter. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 75 mg (33%) of 22c, mp 121-122 °C (mixture melting point),<sup>1</sup> after recrystallization from methanol. Further elution with a mixture (2:3) of benzene and petroleum ether gave 18 mg (90% recovery) of DCN, mp 210-211 °C (mixture melting point), after

recrystallization from methanol. Continued elution of the column with a mixture (1:1) of benzene and petroleum ether gave 80 mg (35%) of the unchanged starting material (18c), mp 170-171 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether. Further elution of the column with benzene gave 60 mg (23%) of 24c, mp 124-125 °C (lit.<sup>1</sup> mp 124-125 °C), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

II.4.11 Thermolysis of 3-Benzyl-3,5-diphenyl-2(3H)-furanone (2a). A sample of 2a (100 mg, 0.31 mmol) was heated at 250 °C for 2 h in a sealed tube. The residue was extracted with dichloromethane, treated with animal charcoal and crystallized from methanol to yield 60 mg (60%) of 5-benzyl-3,5-diphenyl-2(5H)-furanone (13a), mp 163-164 °C (mixture melting point).

II.4.12 Thermolysis of 3-Benzyl-3-(4-methylphenyl)-5-phenyl-2(3H)-furanone (2b). A sample of 2b (100 mg, 0.29 mmol) was thermolysed at 250 °C for 2 h. Extraction of the residue with dichloromethane, followed by workup as in the earlier case gave 80 mg (80%) of 13b, mp 140-141 °C (mixture melting point), after recrystallization from methanol.

II.4.13 Thermolysis of 3-Benzyl-3-(4-methoxyphenyl)-5-phenyl-2(3H)-furanone (2c). A sample of 2c (100 mg, 0.29 mmol) was thermolysed for 2 h at 250 °C and worked up as in the earlier cases to give 75 mg (75%) of 13c, mp 153-154 °C (mixture melting point), after recrystallization from methanol.

II.4.14 Thermolysis of 3,3-Dibenzyl-5-phenyl-2(3H)-furanone (2d). A sample of 2d (100 mg, 0.29 mmol) was heated at 250 °C for 2 h. Extraction of the residue with dichloromethane, followed by workup as in the earlier cases gave 70 mg (70%) of 3,5-dibenzyl-5-phenyl-2(5H)-furanone, mp 135-136 °C (mixture melting point), after recrystallization from methanol.

II.4.15 Fluorescence Measurements.<sup>12</sup> The steady-state fluorescence and quantum yields were measured in a SLM photon counting spectrofluorimeter (SPC 823 + SMC 220). It consists of a xenon arc lamp (OSRAM XBO 450 W/2), a dual excitation monochromator (MC 640, with concave holographic gratings), a pair of detection assemblies, each consisting of a single, analysing monochromator (MC 320, with a holographic grating) and an EMI 9635 QA photomultiplier tube (PMT). The excitation and detection were at right angles to one another. Fluorescence was measured in square (1 cm x 1 cm)

cells of suprasil quartz, using a bandpass of 1-2 mm for the exciting light and 1-4 mm for the emitted light.

II.4.16 Laser Flash Photolysis.<sup>12</sup> For laser flash photolysis, excitation was carried out in a front-face configuration, using 337.1 nm laser pulses (8 ns, 2-3 mJ) from a Molelectron UV-400 system or 425 nm laser pulses (6 ns, 2-10 mJ), generated by pumping a methanolic solution of stilbene 420 (Exciton) with the output at third harmonic (354 nm) from a Quanta-Ray Nd-YAG system. The details of the kinetic spectrometer and computerized data collection system are available elsewhere.<sup>26</sup> Rectangular quartz cells with 2 or 3 mm path lengths along the direction of the analysing light were used for laser flash photolysis. Deoxygenation of solutions was effected by saturating them with argon.

II.5 REFERENCES

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## CHAPTER III

### PHOTOCHEMICAL TRANSFORMATIONS OF A FEW 2H-1,2,4-BENZOTHIADIAZINE 1,1-DIOXIDES

#### III.1 ABSTRACT

Ring enlargement reactions of a few 2H-1,2,4-benzothiadiazine 1,1-dioxides such as 2H-1,2,4-benzothiadiazine-2-(4-methoxyphenyl)-3-methyl 1,1-dioxide (4b), 2H-1,2,4-benzothiadiazine-2-(4-carbomethoxyphenyl)-3-methyl 1,1-dioxide (4c) and 2H-1,2,4-benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-dioxide (4d) have been studied by steady-state irradiation, product analysis and laser flash photolysis. Irradiations of 4b-d in benzene and methanol gave moderate yields (14-70%) of the dibenzothiadiazocine derivatives 9b-d. The product formation may take place either by a concerted process or through a pathway involving a diradical intermediate leading to an intermediate 8, which could rapidly isomerize to the photoproduct 9. Laser flash photolysis under direct excitation (266 and 308 nm) gave long-lived transients, characterized by weak absorptions at 315-420 nm, assigned to either 5 or 8. Both benzophenone and p-methoxyacetophenone triplets were quenched by the

benzothiadiazine dioxides with rate constants (0.58 - 7.8)  $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . The triplets were also shown to be photo-reactive in the ring enlargement reaction.

### III.2 INTRODUCTION

Several examples of the photochemical and thermal transformations of heterohexa-1,3,5-trienes are reported in the literature.<sup>1</sup> Heterohexa-1,3,5-trienes containing hetero atoms such as oxygen, nitrogen and sulphur can, in principle, undergo thermal electrocyclic reactions to give heterocyclohexa-1,3-dienes through a  $[\pi^2_s + \pi^2_s + \pi^2_s]$  process or a  $[\pi^4_a + \pi^2_a]$  type of addition to give heterobicyclo[3.1.0]hexenes.<sup>1</sup> The same heterobicyclo[3.1.0]-systems would be predicted to be formed by the photocyclizations of the corresponding heterohexa-1,3,5-trienes through a  $[\pi^4_a + \pi^2_s]$  or  $[\pi^4_s + \pi^2_a]$  type of addition. In addition to the above cyclizations, monocyclic five-membered rings can be formed from heterohexa-1,3,5-trienes through either a pentadienyl anion mode of cyclization<sup>2</sup> or an intramolecular nucleophilic addition involving hetero atoms such as nitrogen to the heterodiene part of the triene system.<sup>3</sup>

There has been hardly any report so far on the photochemical or thermal transformations of 2H-1,2,4-benzothiadiazines, which could be viewed as precursors of heterohexa-

1,3,5-trienes, containing one sulphur and two nitrogen atoms. In this context, we have examined the photochemical transformations of a few 2H-1,2,4-benzothiadiazine 1,1-dioxides. Preliminary investigations in this laboratory<sup>4</sup> have shown that 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl 1,1-dioxide (4a) on irradiation undergoes ring enlargement to give 5H-dibenzo[b,g][1,4,6]thiadiazocine-6-methyl 12,12-dioxide (9a). The present investigation has been undertaken to examine the generality of such photoreactions and also to study the effect of substituents in the phenyl ring at the C-2 position of the benzothiadiazine moiety in influencing the course of these photoreactions. Laser flash photolysis studies of several of these compounds have also been carried out in order to characterize the transients involved in these phototransformations. The substrates we have examined in the present study under steady-state irradiation include, 2H-1,2,4-benzothiadiazine-2-(4-methoxyphenyl)-3-methyl 1,1-dioxide (4b), 2H-1,2,4-benzothiadiazine-2-(4-carbomethoxyphenyl)-3-methyl 1,1-dioxide (4c), 2H-1,2,4-benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-dioxide (4d) and 2H-1,2,4-benzothiadiazine-2-(2,6-dimethylphenyl)-3-methyl 1,1-dioxide (4e). For laser flash photolysis studies, besides these substrates (4b-e), a few others such as 2H-1,2,4-benzothiadiazine-3-methyl-2-phenyl

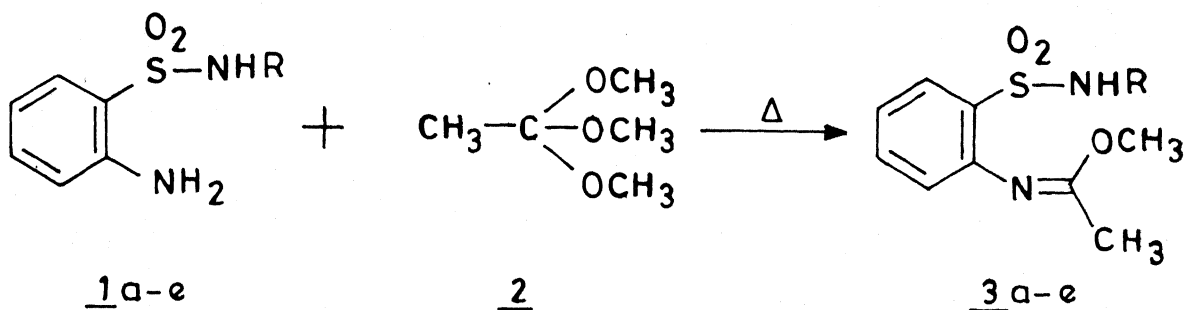
1,1-dioxide (4a), 2H-1,2,4-benzothiadiazine-3-methyl-2-(2-methylphenyl) 1,1-dioxide (4f) and 2H-1,2,4-benzothiadiazine-3-methyl-2-(4-methylphenyl) 1,1-dioxide, (4g) have also been employed.

### III.3 RESULTS AND DISCUSSION

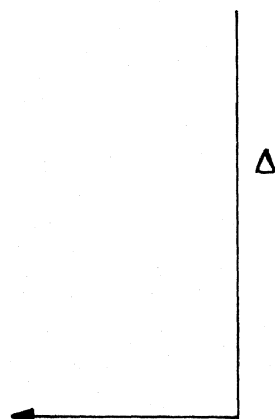
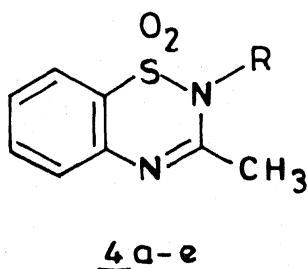
III.3.1 Starting Materials. The thiadiazine dioxides 4b-e were prepared by a slight modification of the earlier procedure,<sup>5</sup> as indicated in Scheme III.1. The structures of all these compounds have been established on the basis of analytical results and spectral evidence. For example, the IR spectra of all these compounds showed a strong absorption around  $1600\text{ cm}^{-1}$ , indicating thereby the presence of a C=N group. In addition, characteristic absorptions of the  $\text{SO}_2$  group ( $1150\text{-}1230$  and  $1300\text{-}1350\text{ cm}^{-1}$ ) were also observed in the IR spectra. The  $^1\text{H}$  NMR spectra of all these compounds showed a singlet at around  $\delta\ 2.0$  (3 H), assigned to the C-2 methyl group. The aromatic protons, in each case, appeared as a multiplet centred around  $\delta\ 7.0\text{-}7.5$  (see experimental section).

III.3.2 Preparative Photochemistry and Product Identification. Irradiation of a solution of 4b in benzene gave a 43% yield of 5H-dibenzo[b,g][1,4,6]thiadiazocine-2-methoxy-6-methyl 12,12-dioxide (9b), in addition to a 33% recovery

# Scheme III.1



- a**,  $R = C_6H_5$   
**b**,  $R = \textit{p}-CH_3OC_6H_4$   
**c**,  $R = \textit{p}-CH_3OCOC_6H_4$   
**d**,  $R = 1\text{-naphthyl}$   
**e**,  $R = 2,6(CH_3)_2C_6H_3$

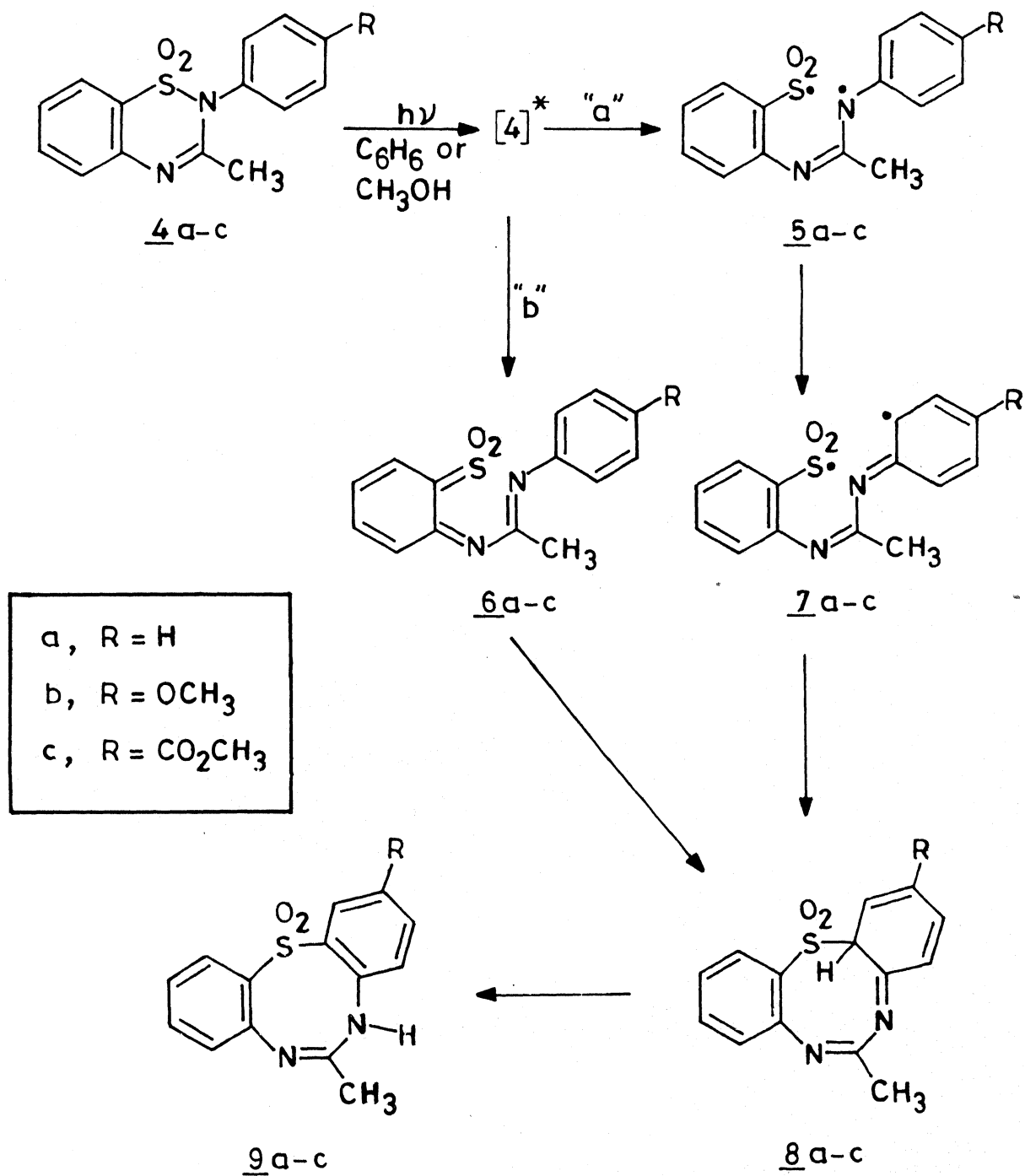


of the unchanged starting material (Scheme III.2). Irradiation of 4b in methanol, on the other hand, gave a 25% yield of 9b, along with a 41% recovery of the unchanged starting material. When the irradiation of 4b was carried out in benzene solution in the presence of acetophenone as sensitizer, under conditions wherein the sensitizer absorbed most of the light, a 40% yield of 9b was obtained, along with a 30% recovery of the unchanged starting material.

Similarly, irradiation of a solution of 4c in benzene gave the ring expansion product, 5H-dibenzo[b,g][1,4,6]thiadiazocine-2-carbomethoxy-6-methyl 12,12-dioxide (9c) in a 70% yield. Irradiation of 4c in methanol, under analogous conditions, gave a 50% yield of 9c. A similar ring enlargement product 9d was obtained in the case of the naphthyl derivative 4d also, though in lower yields. Irradiation of 4d in benzene and methanol gave 9d in 28% and 14% yields, respectively. Substantial amounts of the unchanged starting materials were also recovered in all these reactions.

The effect of blocking both the ortho positions of the 2-phenyl group in such reactions was also investigated by studying the photoreaction of 4e. Thus, when 4e was irradiated in benzene under an RPR light source, no ring expansion product could be isolated; instead, a 20% yield of a

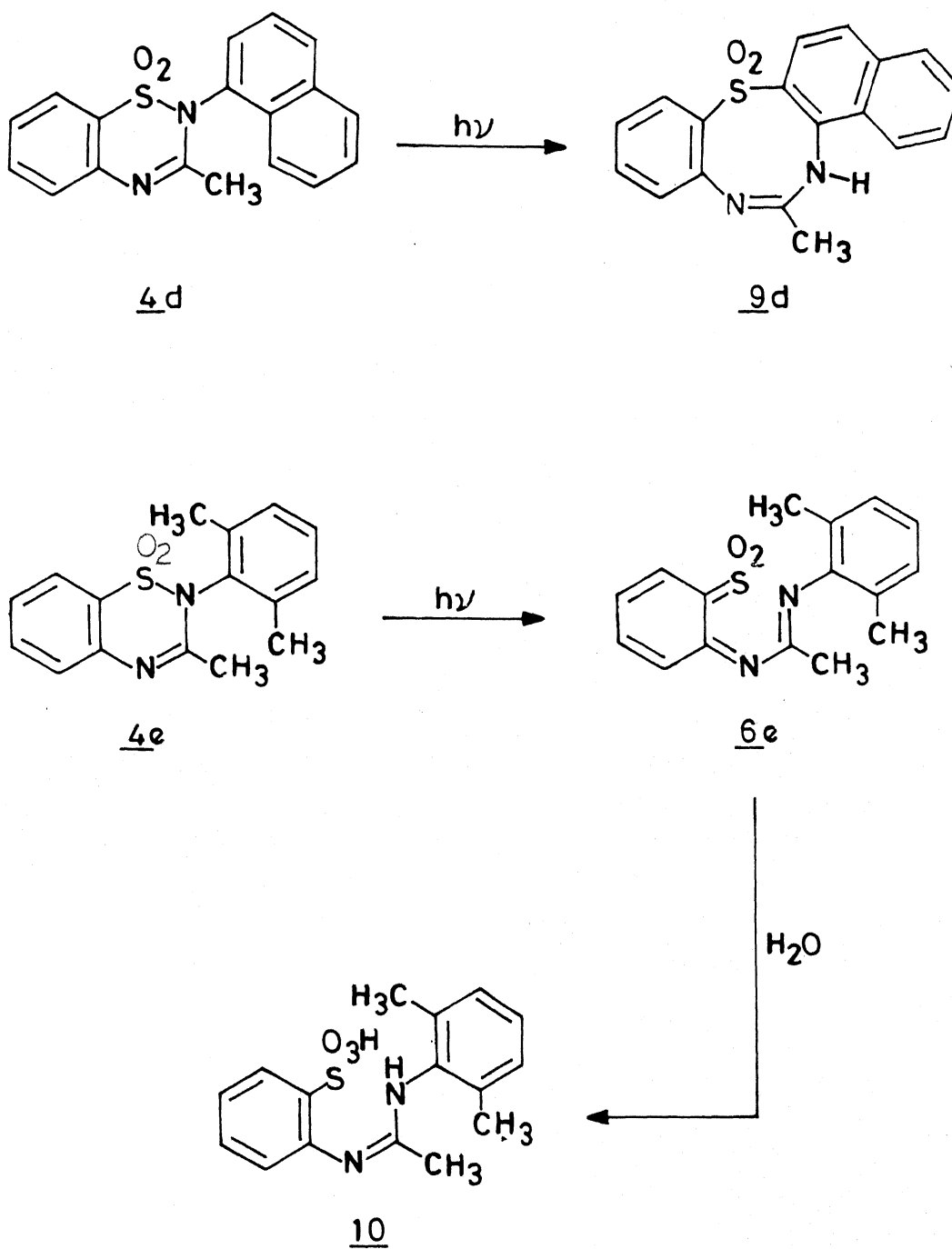
# Scheme III.2





product, tentatively assigned as 10 was obtained, along with a 63% recovery of the unchanged starting material. On the other hand, when the reaction of 4e was carried out in acetone using a Hanovia medium pressure mercury lamp, a nearly quantitative yield of 10 was obtained (Scheme III.3).

The structures of the photoproducts 9b-d were established on the basis of analytical results and spectral evidence. The IR spectra of all these compounds, for example, showed a sharp NH absorption, around  $3320\text{ cm}^{-1}$ . Absorptions corresponding to C=N, as well as,  $\text{SO}_2$  were also observed (see experimental section). The  $^1\text{H}$  NMR spectra of all these compounds were also in agreement with the assigned structures. For example, the  $^1\text{H}$  NMR spectrum of 9d showed a singlet at  $\delta\ 2.5$  (3 H), assigned to the methyl group at the 8-position. (Figure III.1). The aromatic protons appeared as a multiplet centred around  $\delta\ 7.45$  (9 H). The C-13 proton appeared as a doublet of doublets ( $J_{12,13} = 8\text{ Hz}$ ,  $J_{11,13} = 2\text{ Hz}$ ) and the NH, as a broad singlet at  $\delta\ 8.4$  (1 H,  $\text{D}_2\text{O}$ -exchangeable). The structure of 10 was assigned on the basis of preliminary X-ray diffraction studies. This compound was insoluble in most of the organic solvents and hence some of the spectral data could not be obtained.

Scheme III.3

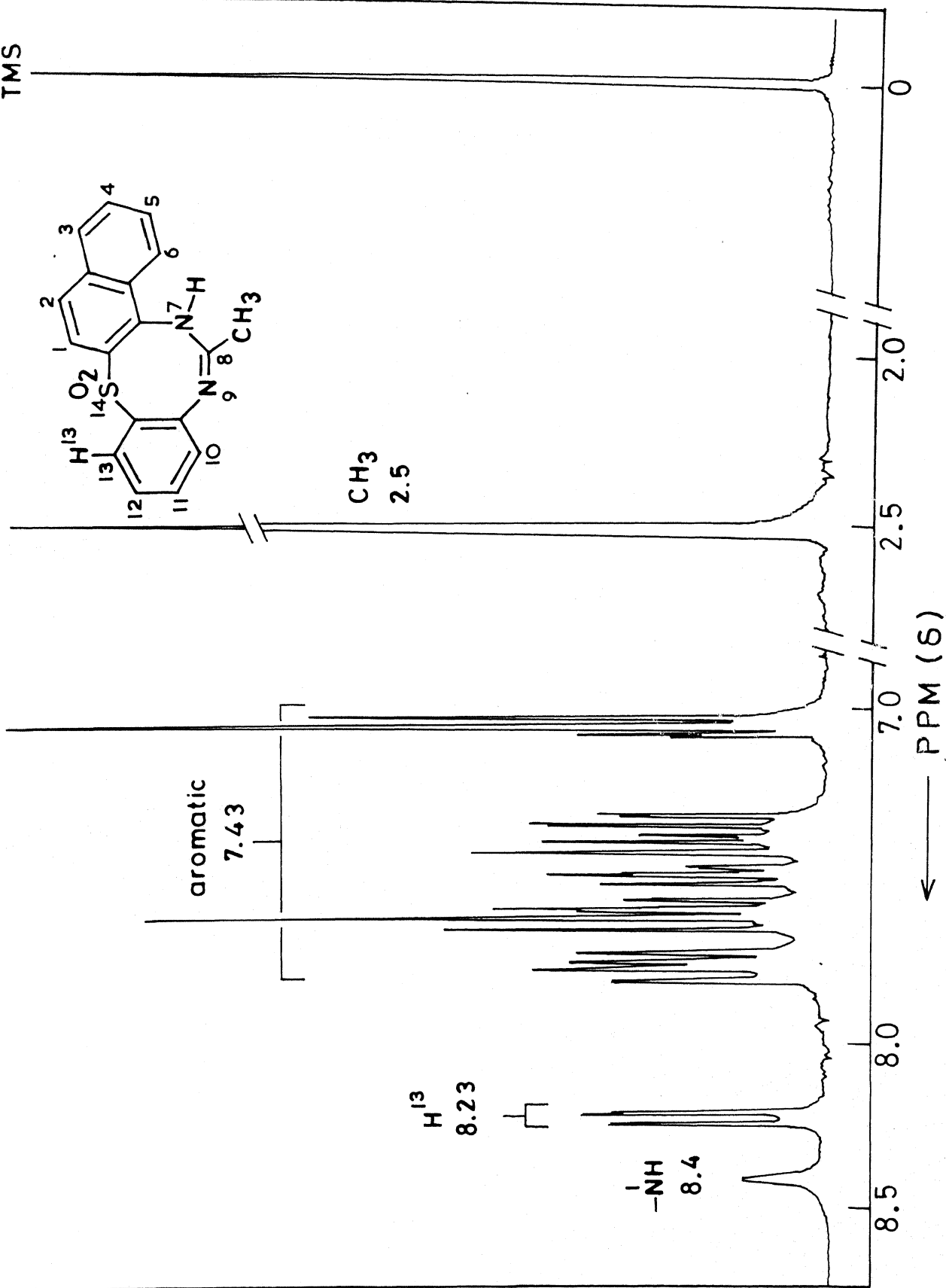


Figure III.1  $^1\text{H}$  NMR spectrum (270MHz) of **8d**.

Discussion. The formation of the different dibenzothiadiazocine dioxides 9b-d in the phototransformations of the corresponding benzothiadiazine dioxides 4b-d could be rationalized in terms of either of the two pathways shown in Scheme III.2. Path 'a' involves a homolytic cleavage of the S-N bond giving the diradical intermediate 5, which in turn, could lead to a second diradical intermediate 7. Coupling of the radical centres in 7 could lead to the intermediate 8. Alternatively, 8 can also be formed through path 'b', involving a concerted ring opening to give 6, followed by ring closure. Further transformation of 8 will lead to the ring expanded product 9. When both the ortho positions of the 2-phenyl ring are blocked by methyl groups, as in the case of 4e, ring closure to the 8-membered ring cannot take place. Instead, addition of elements of water leading to the formation of 10 has been observed (Scheme III.3). It may be pointed out in this connection that Kamigata et al.<sup>6a,b</sup> have recently shown that 2-aryl-1,2-benzisothiazolinones undergo ring expansion reactions on irradiation and the reaction in these cases has been assumed to proceed through diradical intermediates, analogous to 5 and 7 (Scheme III.2). Also, they have shown that 2-pyridyl and 2-pyrazinyl-1,2-benzisothiazol-3(2H)-ones undergo ring enlargement reaction leading to the corresponding seven-membered ring systems.<sup>6c</sup>

It is pertinent to note that when the phenyl group at the 2-position of the thiadiazine moiety carries either electron-donating or withdrawing substituents as in 4b and 4c, respectively, facile ring enlargement reactions leading to the corresponding dibenzothiadiazocines 9b and 9c are observed. When the phenyl group at the 2-position is replaced by a 1-naphthyl group as in 4d, the photoreaction leading to 9d is considerably slowed down. Steric factors may be responsible for the poor yield of the photoproduct in this case. The exact role of the substituent effects on these rearrangements is, however, not fully understood yet.

III.3.3 Laser Flash Photolysis Studies.<sup>7</sup> The benzo-thiadiazine dioxides 4a-d,f,g were subjected to laser flash photolysis under direct excitation at 308 nm (in benzene and methanol) and 266 nm (in methanol), as well as under sensitization by benzophenone and p-methoxyacetophenone (in benzene and acetonitrile). At millimolar concentrations, these substrates have negligible absorptions at > 320 nm; this renders the sensitization experiments feasible under 337.1 and 355 nm laser excitation. However, in the latter experiments, the short wavelength spectral region remains inaccessible for the purpose of the monitoring of photoproduct absorption because of laser scatter and/or

sensitizer and substrate ground-state absorptions.

Upon 308 nm laser flash photolysis in methanol, the substrates under study produce long-lived transient photoproducts absorbing weakly at 315-420 nm ( $\lambda_{\text{max}}^{\text{P}} = 325-350 \text{ nm}$ ).<sup>8</sup> Some of the transient absorption spectra are illustrated in Figure III.2, parts A-D. Compared to the other substrates,  $\lambda_{\text{max}}^{\text{P}}$  in the case of 4b is conspicuously red-shifted (350 nm). The photoproduct spectrum in the case of 4c (Figure III.2, part D) keep on rising, on going to shorter wavelengths and fail to show any maximum in the spectral region of 315-700 nm. The photoproducts undergo slight decay ( $\leq 20\%$ ) on the longest time scale ( $\sim 150 \mu\text{s}$ ). Their decay kinetics as well as yields remain unaffected in the presence of oxygen ( $\sim 2 \text{ mM}$ ). Laser flash photolysis at 308 nm in benzene and at 266 nm in methanol gave essentially similar results, except that the photoproduct spectra in benzene are more extended into the visible ( $\leq 500 \text{ nm}$ ) region.

The insensitivity of the yields and decay kinetics of photoproducts towards oxygen strongly suggests that these are not the triplets of the substrates and that the latter, if long-lived, are not involved as intermediates for the photoproducts under direct excitation. In view of the long-lived character ( $\tau > 500 \mu\text{s}$ ) of the transient absorptions, it was important to examine critically if there were

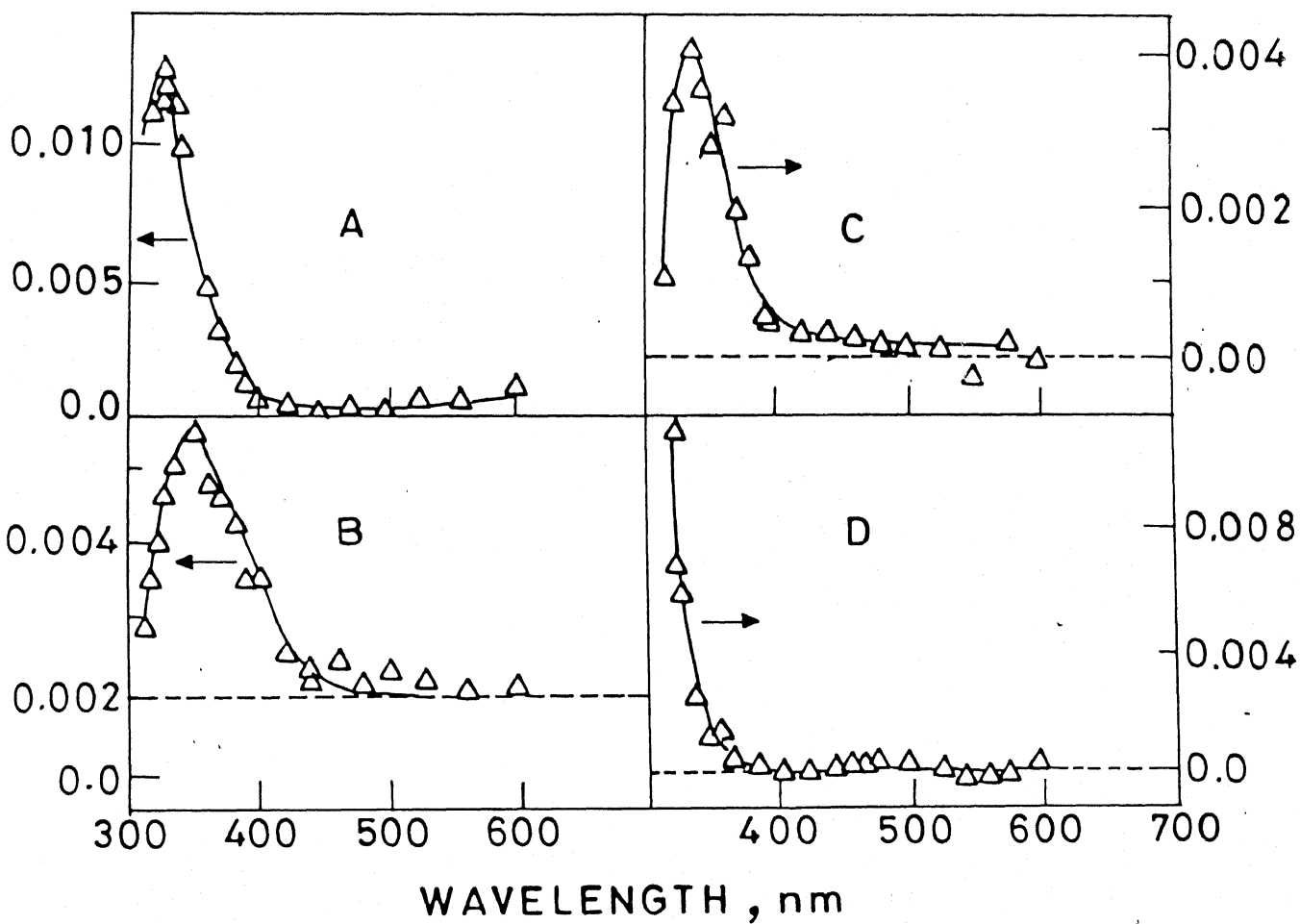


Figure III.2 Photoproduct absorption spectra at 3-5  $\mu$ s following 308 nm laser flash photolysis of (A) 4a, (B) 4b, (C) 4d and (D) 4c.

substantial contributions from the final isolated products (i.e., 9), formed via a fast route. For this purpose, we have recorded the permanent absorption spectral changes upon partial photolysis of the substrates using 308 nm laser pulses (repetitive, 10 Hz). A few representative cases are presented in Figure III.3. The product spectra are characterized by long-wavelength band systems ( $\lambda_{\text{max}}$ 's in benzene = 338 and 392 nm for products from 4d and ~ 365 nm for others). A comparison with the absorption spectra of the isolated ring expanded products (dibenzothiadiazo-cine dioxides) reveals that these compounds and the unreacted substrates are the principal components of the partially photolysed mixtures from 308 nm laser irradiation. Although the existence of the long-wavelength absorption band-systems at 330-460 nm for the ring expanded products and observation of absorptions due to laser-flash-photolytic, long-lived photoproducts in the same region suggest a link between the two, a close scrutiny shows that they are not related. For example, the substituents ( $\text{OCH}_3$  vs.  $\text{COOCH}_3$ ) at the 2-position of dibenzothiadiazo-cine dioxides do not make any difference in the location of the low-energy  $\lambda_{\text{max}}$  of the products of photolysis (365 nm in benzene); however, the transient photoproduct spectra



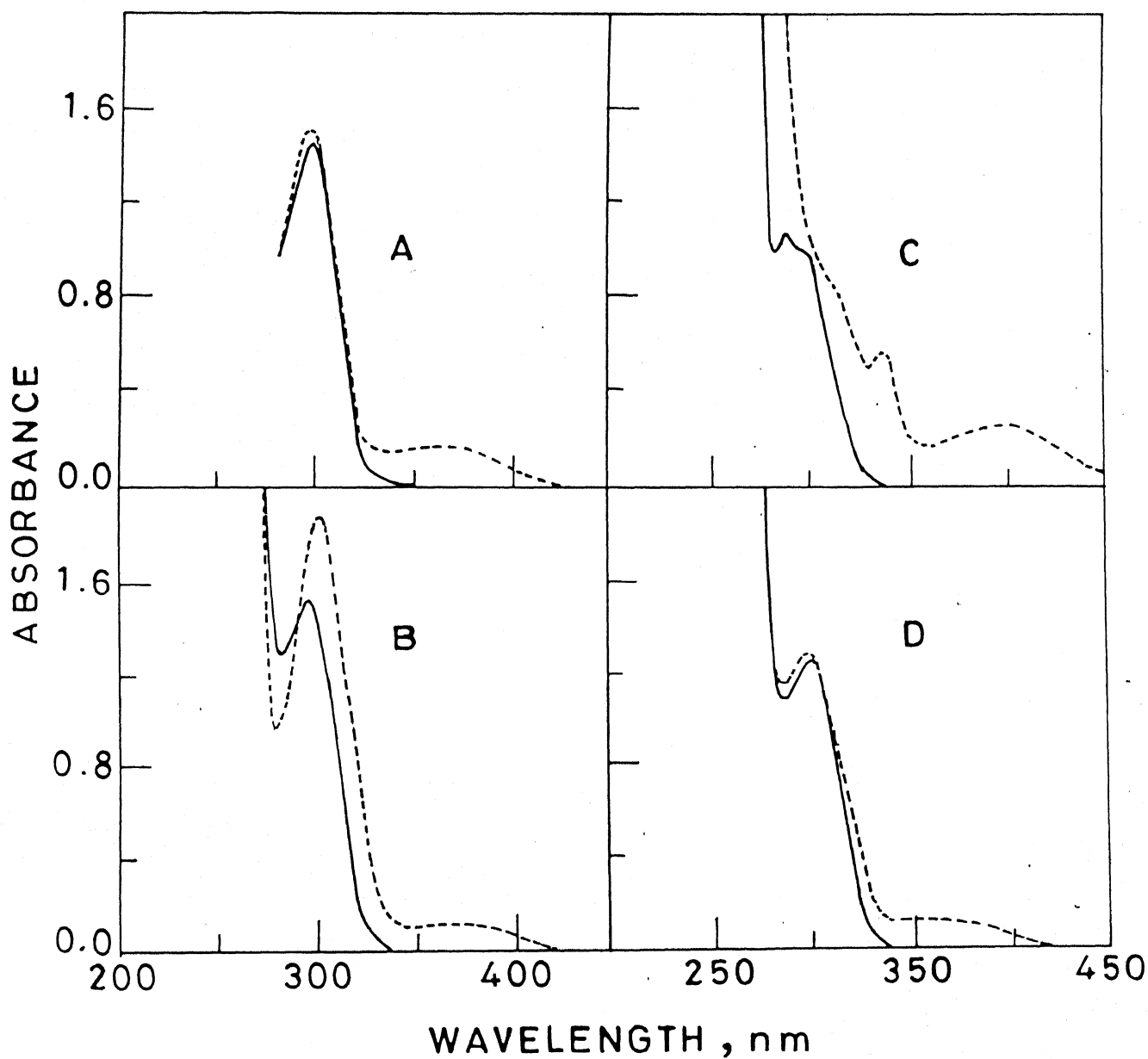


Figure III.3 Permanent spectral changes observed upon irradiation (5 min) of (A) 4a, (B) 4b, (C) 4d and (D) 4c by repetitive 308 nm laser pulses. The continuous and dotted curves represent absorption spectra before and after irradiation, respectively.

seen upon laser flash photolysis show a substantial difference ( $\lambda_{\text{max}} = 350 \text{ nm}$  vs.  $< 315 \text{ nm}$  for 4b vs. 4f in methanol). Similarly, in the case of the 1-naphthyl derivative 4d, the two-band feature of the spectrum of the isolated product 9d is absent in the laser-pulse-induced transient spectra. In view of this spectral dissimilarity, as well as the transient nature of the absorption, we are led to the conclusion that the final ring expanded products are not responsible for the absorption changes at  $\leq 150 \mu\text{s}$  following laser flash photolysis. Plausible assignments for the latter may be sought in terms of the diradical 5 or the intermediate 8 (in the light of the photochemistry observed under steady-state irradiation).

The thiadiazine dioxides prove to be moderate to efficient quenchers for benzophenone (BP) and p-methoxyacetophenone (PMA) triplets. The bimolecular rate constants ( $k_q^T$ ) for quenching, obtained from the linear dependence of the pseudo-first-order rate constants (for ketone triplet decay) on substrate concentrations are compiled in Table III.1. The BP and PMA triplets were produced by excitation with 337.1 nm laser pulses and monitored by their absorptions 520-530 nm and 370-380 nm, respectively. From the kinetic data, it is not obvious if the mechanism of the

Table III.1 Transient Photoproduct Maxima ( $\lambda_{\max}^P$ ) upon 308 nm Laser Excitation of 4a-d,g,f in Methanol, and Bimolecular Rate constants ( $k_q^T$ ) for the Quenching of Benzophenone (BP) and p-Methoxyacetophenone (PMA) Triplets by these Substrates in Benzene and Acetonitrile.

Quencher	$\lambda_{\max}^P$ , nm <sup>a</sup>	$k_q^T$ , $10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>b</sup>			
		$^3\text{BP}^*/\text{Bz}$	$^3\text{PMA}^*/\text{Bz}$	$^3\text{BP}^*/\text{MeCN}$	$^3\text{PMA}^*/\text{MeCN}$
<u>4a</u>	325	0.67	3.4	1.2	3.8
<u>4b</u>	350	0.81	3.5	1.2	3.8
<u>4c</u>	< 315	0.57	3.3	1.3	3.9
<u>4d</u>	330	4.30	5.6	6.1	7.8
<u>4f</u>	330	0.58	3.0	0.85	3.4
<u>4g</u>	330	0.68	3.3	1.2	3.5

<sup>a</sup>  $\pm 5$  nm

<sup>b</sup> ca.  $\pm 15\%$

quenching is charge transfer or energy transfer. However, the lack of observation of ketyl radical ( $\lambda_{\text{max}} = 545 \text{ nm}$ ) or radical anion (600–700 nm) in the course of the quenching of BP triplet in benzene and acetonitrile points against a charge transfer mechanism with the substrates acting as electron donors. On the other hand, the fact that  $k_q^T$  increases on going from BP ( $E_T = 69 \text{ kcal mol}^{-1}$ )<sup>9</sup> to PMA ( $E_T = 72 \text{ kcal mol}^{-1}$ )<sup>9</sup> is compatible with an energy transfer mechanism.

As evident from Table III.1,  $k_q^T$ 's in both benzene and acetonitrile are much higher for 4d than for other substrates. Understandably, the naphthyl group ( $E_T$  for naphthalene =  $61 \text{ kcal mol}^{-1}$ )<sup>9</sup> provides an exothermic energy transfer pathway for quenching. The transient absorption spectrum (Figure III.4, parts A and A') of the product of quenching of the ketone triplets by 4d has its maximum at 420 nm (in benzene) and resembles, in both appearance and location, the triplet-triplet absorption spectrum of naphthalene ( $\lambda_{\text{max}} = 423 \text{ nm}$  in benzene).<sup>10</sup> It is quenched by oxygen with a rate constant of  $8.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (in benzene). The most reasonable assignment for the 420 nm species is that it is triplet of 4d with the excitation energy localized primarily on the naphthyl moiety. The fact that this transient is not

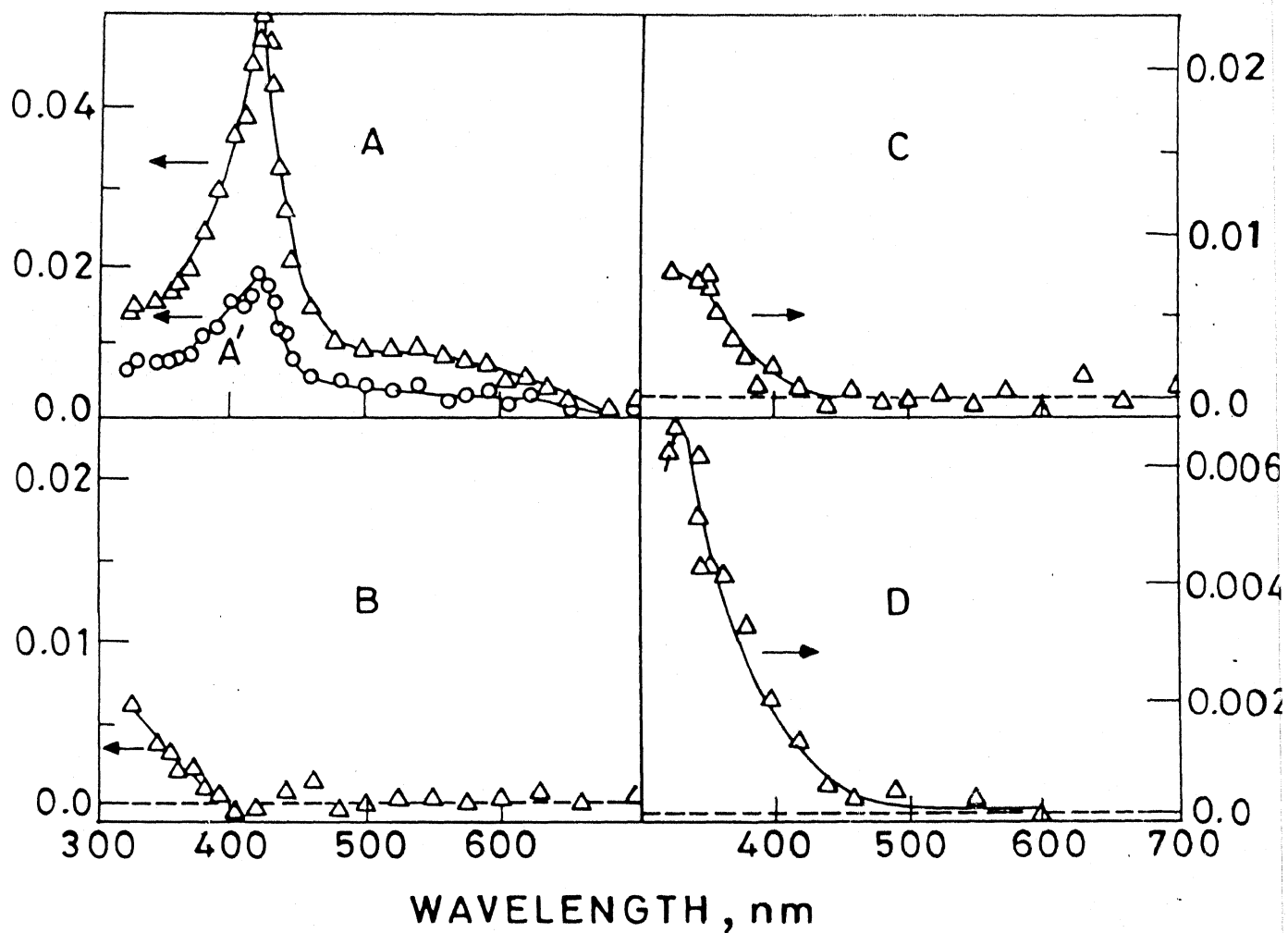


Figure III.4 Transient absorption spectra at 1 (A), 7 (A'), 3 (B) and 5 (C,D)  $\mu$ s following 337.1 nm laser excitation of p-methoxyacetophenone in the presence of (A,A') 4d, (B) 4a, (C) 4f and (D) 4b in benzene.

observed as a result of the direct laser excitation (266 or 308 nm) of 4d in methanol suggests that the intersystem crossing quantum yield is negligible for this system. While the relatively short lifetime (5.6  $\mu$ s in benzene) of the triplet of 4d suggests its photo-active nature (see below), no growth component concomitant with its decay is observed at short wavelengths (Figure III.4, parts A and A').

The decay of PMA triplet under efficient quenching by the thiadiazine dioxides leads to weak, but nonnegligible, residual absorptions with spectral and kinetic features reminiscent of those seen under direct laser excitation. The transient spectra in three cases are shown in Figure III.4 parts B-D. The insensitivity of the decay of these transient absorptions towards oxygen rules out their assignments in terms of the triplets of the substrates or ketyl radical derived from PMA. It is possible that these correspond to the same species seen under direct laser excitation. It is worthwhile to note that the photolysis of PMA in benzene containing 1 mM 4b and 4d by repetitive 355 nm laser pulses leads to accumulation of the photoproducts 9b and 9d. This is evident from the development of the characteristic long-wavelength band systems of the latter at 330-400 nm. This establishes that the

triplets of 4b,d as well as those of the other substrates (by analogy), are photoreactive as far as the ring enlargement reaction is concerned. A similar conclusion has also been arrived at on the basis of acetophenone sensitized, steady-state photolysis of 4b in benzene (vide supra).

### III.4 EXPERIMENTAL SECTION

All melting points are uncorrected and were determined on a Mel-Temp apparatus. The IR spectra were recorded on either Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D, Cary 219 or Beckmann DB spectrophotometers. The  $^1\text{H}$  NMR spectra were recorded on Varian EM-390 or Bruker 270 MHz spectrometers, using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E single focussing mass spectrometer or a Varian Mat CH7 mass spectrometer at 70 eV. Steady-state irradiations were carried out in a Srinivasan-Griffin-Rayonet photochemical reactor (RPR 3000 or 3500 Å) or using a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketed immersion well.

III.4.1 Starting Materials. Trimethyl orthoacetate (2),<sup>11</sup> bp 107-109 °C, N-(2-aminobenzenesulphonyl)-1-naphthylamine (1a),<sup>5</sup> mp 128-129 °C, N-(2-aminobenzenesulphonyl)-

2,6-dimethylaniline (1e),<sup>5</sup> mp 144-145 °C and 2-nitrobenzenesulphonyl chloride,<sup>12</sup> mp 64-65 °C were prepared by reported procedures. Solvents for steady-state photolysis studies were purified and distilled before use, whereas Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60-80 °C.

III.4.2 Preparation of 2H-1,2,4-Benzothiadiazine  
1,1-Dioxides 4b-e. The thiadiazine dioxides 4b-e were prepared by slightly modifying the procedure adopted by Freeman and Wagner.<sup>5</sup>

2H-1,2,4-Benzothiadiazine-2-(4-methoxyphenyl)-3-methyl  
1,1-Dioxide (4b). To a mixture of pyridine (3.08 g, 40 mmol) and p-anisidine (4.92 g, 40 mmol) was added 2-nitrobenzenesulphonyl chloride (8.84 g, 40 mmol) in small portions, over a period of 0.5 h, with stirring. The reaction mixture was subsequently warmed to around 60-70 °C for 0.5 h and was then treated with dilute hydrochloric acid (2 N, 150 mL). The residue obtained was crystallized from a mixture (1:1) of benzene and petroleum ether to give 8.42 g (68%) of N-(2-nitrobenzenesulphonyl)-4-methoxyaniline, mp 106-107 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3260 (NH), 3100, 3080, 3025, 2960 (CH), 1590, 1540 (C=C), 1360 and 1170 (SO<sub>2</sub>) cm<sup>-1</sup>.

To a hot solution of N-(2-nitrobenzenesulphonyl)-4-metho-



xylaniline (6.16 g, 20 mmol) in glacial acetic acid (50 mL), maintained around 85 °C, was added zinc powder (4 g) in small portions over a period of 15 minutes. The mixture was cooled, filtered and poured over crushed ice. The solid that separated out was washed with water and recrystallised from a mixture (3:2) of benzene and petroleum ether to give 3.34 g (60%) of N-(2-aminobenzenesulphonyl)-4-methoxyaniline (1b), mp 96-97 °C.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3485, 3390 (NH<sub>2</sub>), 3220 (NH), 3070, 3040, 2980, 2940 (CH), 1630, 1600 (C=C), 1330 and 1145 (SO<sub>2</sub>) cm<sup>-1</sup>.

A mixture of N-(2-aminobenzenesulphonyl)-4-methoxyaniline (1b, 2.8 g, 10 mmol) and trimethyl orthoacetate (1.56 g, 13 mmol) was heated around 130-140 °C for 0.5 h. The excess orthoacetate was removed under vacuum and the residue was crystallized from a mixture (1:1) of benzene and petroleum ether to give 2.8 g (80%) of 3b, mp 102-103 °C.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3270 (NH), 3060, 3030, 3010, 2980, 2940, 2850 (CH), 1640 (C=N), 1590 (C=C), 1340 and 1170 (SO<sub>2</sub>) cm<sup>-1</sup>.

A solution of 3b (1.65 g, 2 mmol) in o-dichlorobenzene (25 mL) was refluxed for 2 h and the solvent was removed under vacuum to give a residue, which was washed with

petroleum ether and recrystallized from a mixture (1:1) of benzene and petroleum ether to give 1.52 g (93%) of 2H-1, 2,4-benzothiadiazine-2-(4-methoxyphenyl)-3-methyl 1,1-dioxide (4b), mp 171-172 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3040, 3000, 2955, 2820 (CH), 1600 (C=N), 1525 (C=C), 1320 and 1160 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 251 nm ( $\epsilon$ , 14,800), 266 (15,000), 295 (94,000).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.1 (s, 3 H, methyl), 3.8 (s, 3 H, methoxy) and 7.3 (m, 8 H, aromatic).

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S: C, 59.68; H, 4.63; N, 9.27. Found: C, 59.52; H, 4.59; N, 9.23.

2H-1,2,4-Benzothiadiazine-2-(4-carbomethoxyphenyl)-3-methyl 1,1-Dioxide (4c). To a stirred mixture of pyridine (1.2 g, 15 mmol) and methyl p-aminobenzoate (2.25 g, 15 mmol) was added 2-nitrobenzenesulphonyl chloride (3.31 g, 15 mmol) in small portions over a period of 0.5 h at room temperature, after which time the mixture was warmed to around 60-70 °C. Workup of the reaction mixture as in the earlier case gave 3.1 g (62%) of N-(2-nitrobenzenesulphonyl)-4-carbomethoxyaniline, mp 199-200 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\max}$  (KBr): 3220 (NH), 3020, 2930, 2850 (CH), 1680 (C=O), 1600 (C=C), 1345 and 1150 (SO<sub>2</sub>) cm<sup>-1</sup>.

A solution of N-(2-nitrobenzenesulphonyl)-4-carbomethoxyaniline (2.3 g, 6.8 mmol) in glacial acetic acid (50 mL) was reduced with zinc powder (4 g) at 80 °C. Workup of the reaction mixture as in the earlier case gave 1.64 g (78%) of N-(2-aminobenzenesulphonyl)-4-carbomethoxyaniline (1c), mp 174-175 °C, after recrystallization from a mixture (3:2) of benzene and petroleum ether.

IR spectrum  $\nu_{\max}$  (KBr): 3430, 3340 (NH<sub>2</sub>), 3205 (NH), 3040, 3000, 2935, 2850 (CH), 1685 (C=O), 1600 (C=C), 1310 and 1135 (SO<sub>2</sub>) cm<sup>-1</sup>.

Heating of a mixture of 1c (1.53 g, 5 mmol) and trimethyl orthoacetate (1.2 g, 10 mmol) around 115-125 °C for 0.5 h, followed by removal of the unchanged orthoacetate under vacuum and recrystallization of the residue from a mixture (1:1) of chloroform and petroleum ether gave 1.8 g (99%) of 3c, mp 148-149 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3235 (NH), 3040, 3015, 2970, 2920 (CH), 1680 (C=O), 1660 (C=N), 1590 (C=C), 1280 and 1150 (SO<sub>2</sub>) cm<sup>-1</sup>.

Refluxing of 3c (1.75 g, 4.8 mmol) in dry xylene (15 mL) for 2.5 h, followed by removal of xylene and workup

as in the earlier case gave 1.26 g (79%) of 4c, mp 193-194 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3075, 3025, 3000, 2935 (CH), 1710 (C=O), 1600 (C=N), 1570 (C=C), 1320 and 1170 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\text{max}}$  (methanol): 258 nm ( $\epsilon$ , 18,800), 263 (21,700), 296 (11,700).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.16 (s, 3 H, methyl), 3.93 (s, 3 H, carbomethoxy) and 7.71 (m, 8 H, aromatic).

Anal. Calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>S: C, 58.18; H, 4.24; N, 8.48. Found: C, 58.01; H, 4.32; N, 8.50.

2H-1,2,4-Benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-Dioxide (4d). A mixture of N-(2-aminobenzenesulphonyl)-1-naphthylamine 1d (2.24 g, 7.5 mmol) and trimethyl orthoacetate (1.8 g, 15 mmol) was heated around 130-140 °C for 0.5 h. Workup of the reaction mixture as in the earlier cases gave 1.8 g (67%) of 3d, mp 144-145 °C, after recrystallization from a mixture (1:1) of benzene and petroleum ether.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3230 (NH), 3060, 3040, 2940 (CH), 1650 (C=N), 1590 (C=C), 1300 and 1165 (SO<sub>2</sub>) cm<sup>-1</sup>.

3d (1.78 g, 5 mmol) was refluxed in o-dichlorobenzene (25 mL) for 2.5 h. Workup of the reaction mixture as in

the earlier case gave 0.98 g (60%) of 2H-1,2,4-benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-dioxide, mp 154-155 °C after recrystallization from chloroform.

IR spectrum  $\nu_{\max}$  (KBr): 3060, 2930 (CH), 1610 (C=N), 1585 (C=C), 1230 and 1180 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 252 nm ( $\epsilon$ , 16,100), 262 (16,000), 271 (15,900).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.1 (s, 3 H, methyl) and 7.6 (m, 11 H, aromatic).

Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 67.08; H, 4.34; N, 8.69. Found: C, 66.81; H, 4.23; N, 8.97.

2H-1,2,4-Benzothiadiazine-2-(2,6-dimethylphenyl)-3-methyl 1,1-Dioxide (4e). A mixture of N-(2-aminobenzene-sulphonyl)-2,6-dimethylaniline (2.5 g, 9 mmol) and trimethyl orthoacetate (2.2 g, 18 mmol) was heated around 135-140 °C for 2 h. Workup of the reaction mixture as in the earlier cases gave 2.5 g (83%) of 3e, mp 120-121 °C.

IR spectrum  $\nu_{\max}$  (KBr): 3220 (NH), 3070, 3010, 2960, 2920 (CH), 1650 (C=N), 1365 and 1165 (SO<sub>2</sub>) cm<sup>-1</sup>.

A solution of 3e (2.5 g, 7.7 mmol) in *o*-dichlorobenzene (10 mL) was heated to reflux for 5 h and worked up in the usual manner to give 1.70 g (75%) of 2H-1,2,4-benzothiadiazine-2-(2,6-dimethylphenyl)-3-methyl 1,1-dioxide,

mp 180-181 °C, after recrystallization from benzene.

IR spectrum  $\nu_{\max}$  (KBr): 3070, 3020, 2950, 2920 (CH), 1610 (C=N), 1580 (C=C), 1340 and 1180 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 247 nm ( $\epsilon$ , 17,400), 262 (17,900), 294 (9,600).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.12 (s, 3 H, 3-methyl), 2.25 (s, 6 H, 2',6'-methyls) and 7.5 (m, 7 H, aromatic).

Anal. Calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S: C, 63.00; H, 5.33; N, 9.33. Found: C, 63.22; H, 5.50; N, 9.08.

III.4.3 Photolysis of 2H-1,2,4-Benzothiadiazine-2-(4-methoxyphenyl)-3-methyl 1,1-Dioxide (4b). A solution of 4b (302 mg, 1 mmol) in benzene (180 mL) was irradiated for 3 h (RPR, 3000 Å). The experiment was repeated once again, to irradiate in all, 604 mg (2 mmol) of 4b. The solvent was removed under vacuum and the resultant residue was chromatographed over silica gel. Elution with a mixture (3:2) of benzene and petroleum ether gave 200 mg (33%) of the unchanged starting material (4b), mp 172-173 °C (mixture melting point), after recrystallization from a mixture (1:1) of benzene and petroleum ether. Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 260 mg (43%) of 5H-dibenzo[b,g][1,4,6]thiadiazocine-2-methoxy-6-methyl 12,12-dioxide (9b), mp 243-244 °C, after recrystallization from acetone.

IR spectrum  $\nu_{\max}$  (KBr): 3315 (NH), 3090, 3020, 2980, 2950 (CH), 1665 (C=N), 1570 (C=C), 1300 and 1155 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 257 nm ( $\epsilon$ , 15,000), 300 (12,600), 354 (1,200).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.25 (s, 3 H, methyl), 3.75 (s, 3 H, methoxy), 7.3 (m, 6 H, aromatic), 7.6 (doublet of a doublet, 1 H, H-11,  $J_{10,11} = 7$  Hz;  $J_{9,11} = 2$  Hz), 8.16 (broad s, 1 H, D<sub>2</sub>O-exchangeable, NH).

Mass spectrum, m/e (relative intensity): 302 (M<sup>+</sup>, 19), 301 (M<sup>+</sup> - H, 15), 238 (M<sup>+</sup> - SO<sub>2</sub>, 14), 237 (M<sup>+</sup> - SO<sub>2</sub> - H, 86), 236 (M<sup>+</sup> - SO<sub>2</sub> - 2 H, 100), 222 (M<sup>+</sup> - SO<sub>2</sub> - CH<sub>3</sub>, 26), 221 (M<sup>+</sup> - SO<sub>2</sub> - CH<sub>3</sub> - H, 15) and other peaks.

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>S: C, 59.68; H, 4.63; N, 9.27. Found: C, 59.60; H, 4.65; N, 9.13.

In a repeat experiment, a solution of 4b (604 mg, 2 mmol) in methanol (440 mL) was irradiated (RPR, 3000 Å) for 3 h. Workup as in the earlier case gave 250 mg (41%) of the unchanged starting material 4b, mp 171-172 °C (mixture melting point) and 150 mg (25%) of 9b, mp 243-244 °C (mixture melting point).

Acetophenone-sensitized Irradiation of 4b. A solution of 4b (50 mg, 0.16 mmol) in benzene (40 mL) containing acetophenone (500 mg, 4.2 mmol) was photolysed in a pyrex vessel

(RPR, 3500 Å) using a 2 mM solution of naphthalene as filter, for 2 h. Removal of the solvent under vacuum and workup as in the earlier case gave 15 mg (30%) of the unchanged starting material, mp 171-172 °C (mixture melting point) and 20 mg (40%) of 9b, mp 243-244 °C (mixture melting point). In a blank run, a benzene solution of 4b (50 mg, 0.16 mmol in 40 mL) was irradiated in the absence of acetophenone for 2 h, keeping all other conditions identical to the previous run. Removal of the solvent under vacuum and workup of the mixture as in the earlier case gave 40 mg (80%) of the unchanged starting material 4b, mp 171-172 °C (mixture melting point).

III.4.4 Photolysis of 2H-1,2,4-Benzothiadiazine-2-(4-carbomethoxyphenyl)-3-methyl 1,1-Dioxide (4c). A solution of 4c (100 mg, 0.33 mmol) in benzene (180 mL) was irradiated (RPR, 3000 Å) for 10 h. Removal of the solvent under vacuum and recrystallization of the residue from chloroform gave 70 mg (70%) of 5H-dibenzo[b,g][1,4,6]thiadiazocine-2-carbomethoxy-6-methyl 12,12-dioxide, 9c, mp 231-232 °C, after further recrystallization from acetone.

IR spectrum  $\nu_{\max}$  (KBr): 3335 (NH), 3075, 3020, 2940 (CH), 1715 (C=O), 1665 (C=N), 1285 and 1150 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 225 nm ( $\epsilon$ , 18,300), 300 (7,600), 361 (1,900).



$^1\text{H}$  NMR spectrum (acetone- $\text{d}_6$ ):  $\delta$  2.3 (s, 3 H, methyl), 3.8 (s, 3 H, carbomethoxy) and 7.6 (m, 8 H, aromatic and NH).

Anal. Calcd for  $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ : C, 58.18; H, 4.24; N, 8.48. Found: C, 57.79; H, 3.87; N, 8.90.

In another run, a solution of 4c, (50 mg, 0.17 mmol) in methanol (100 mL) was irradiated (RPR, 3000 Å) for 10 h. Removal of the solvent, followed by workup as in the earlier case gave 25 mg (50%) of 9c, mp 231-232 °C (mixture melting point).

III.4.5 Photolysis of 2H-1,2,4-Benzothiadiazine-3-methyl-2-(1-naphthyl) 1,1-Dioxide (4d). A solution of 4d (300 mg, 0.93 mmol) in benzene (220 mL) was irradiated (RPR, 3000 Å) for 4 h. The experiment was repeated once again to irradiate, in all, 600 mg (1.86 mmol) of 4d. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (2:3) of benzene and petroleum ether gave 320 mg (54%) of the unchanged starting material, 4d, mp 154-155 °C (mixture melting point), after recrystallization from chloroform. Further elution of the column with a mixture (4:1) of benzene and petroleum ether gave 172 mg (28%) of 7H-benzo[g]naphtho[2,1-b][1,4,6]thiadiazocine 14,14-dioxide (9d), mp 234-235 °C, after recrystallization from acetone.

IR spectrum  $\nu_{\max}$  (KBr): 3305 (NH), 3090, 3030, 2990 (CH), 1660 (C=N), 1575 (C=C), 1295 and 1160 (SO<sub>2</sub>) cm<sup>-1</sup>.

UV spectrum  $\lambda_{\max}$  (methanol): 256 nm ( $\epsilon$ , 27,800), 262 (34,200), 307 (6,100), 333 (4,300).

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>):  $\delta$  2.5 (s, 3 H, methyl), 7.45 (m, 9 H, aromatic), 8.23 (doublet of a doublet, 1 H, H-13;  $J_{12,13} = 8$  Hz,  $J_{11,13} = 2$  Hz) and 8.4 (s, 1 H, D<sub>2</sub>O-exchangeable, NH).

Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 67.08; H, 4.35; N, 8.70. Found: C, 66.93; H, 4.31; N, 8.52.

In another experiment, a solution of 4d (600 mg, 0.93 mmol) in methanol (440 mL) was irradiated for 5 h (RPR, 3000 Å) and worked up as in the earlier cases to give 360 mg (60%) of the unchanged starting material (4d), mp 154–155 °C (mixture melting point) and 85 mg (14%) of 9d, mp 234–235 °C (mixture melting point).

III.4.6 Photolysis of 2H-1,2,4-Benzothiadiazine-2-(2,6-dimethylphenyl)-3-methyl 1,1-Dioxide (4e). A solution of 4e (300 mg, 1 mmol) in benzene (200 mL) was irradiated (RPR, 3000 Å) for 15 h. Partial removal of the solvent gave a solid product, which was filtered and washed with chloroform to yield 63 mg (20%) of 10, mp 284–286 °C, after recrystallization from methanol.

IR spectrum  $\nu_{\text{max}}$  (KBr): 3140-2600 (NH which may be existing as  $\text{NH}_2^+$ ), 3040, 3010, 2960 (CH), 1640 (C=N), 1580 (C=C), 1240 and 1187 ( $\text{SO}_3^-$ )  $\text{cm}^{-1}$ .

UV spectrum  $\lambda_{\text{max}}$  (methanol): 249 nm ( $\epsilon$ , 15,800), 260 (10,100).

Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ : C, 60.37; H, 5.66; N, 8.81. Found: C, 60.91; H, 5.57; N, 8.51.

The mother liquor after removal of 10, was concentrated and the residue obtained was crystallized from benzene to give 190 mg (63%) of the unchanged starting material, mp 180-181 °C (mixture melting point).

In another experiment, a solution of 4e (600 mg, 2 mmol) in acetone (250 mL) was irradiated for 2 h (Hanovia 450-W). Removal of the solvent under vacuum gave a solid, which was filtered and washed with dichloromethane to give 590 mg (93%) of 10, mp 284-286 °C (mixture melting point), after recrystallization from methanol.

III.4.7 Laser Flash Photolysis.<sup>7</sup> For laser flash photolysis, the pulse excitation was carried out at 337.1 nm (2-3 mJ, ~8 ns, Molelectron UV-400 nitrogen laser), 355-266 nm (< 10 mJ, ~6 ns, Quanta-Ray DCR-1 Nd-YAG, 3rd/4th harmonic) or 308 nm (< 20 mJ, ~20 ns, Lambda-Physik EMG 101 MSC

Excimer). The transient phenomena were observed in terms of absorption in 2-3 mm quartz cells using a kinetic spectrophotometer.<sup>13</sup> The solvents employed were benzene and methanol and the solutions were deoxygenated by purging with argon or nitrogen, except in cases where oxygen effects were to be studied. In the experiments requiring a large number of laser shots (e.g., for wavelength-by-wavelength measurements of transient absorption spectra), a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell.

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## VITAE

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